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- I. *The Deformation of a Bloom Plate resting on an Elastic Base when a Load is transmitted to the Plate by means of a Stanchion.* By J. VINT and W. N. ELGOOD*.

[Plate I,]

EXPERIMENTAL investigations of the behaviour of bloom plates loaded through stanchions and resting on elastic foundations, undertaken mainly in America †, have led to observations from which have been inferred by deduction general rules to govern the practical design of such plates. Nowhere does an attempt appear to have been made to infer by induction from mathematical analysis and observations laws concerning the behaviour of these cases. Experience tends to show that the general rules covering design approximate to the truth, but the designer has to be satisfied with formulæ which are known to have little support from induced laws or theories.

In Part I. of this communication the problem is treated mathematically, while in Part II. the experimental verification of some of the mathematical results is dealt with.

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† G. C. Priester and C. H. Sandberg, 'Engineering News Record,' civ. no. 12 (1931); K. G. Merriam, 'Engineering News Record,' cvii. no. 6 (1931); K. G. Merriam and D. G. Downing, 'Bulletin of American Institute of Steel Construction (Inc.),' Design of Steel Column Slabs, etc.

PART I.

For mathematical purposes we assume the bloom plate to be a uniform thin flat plate to which the elastic theory of thin plates is applicable, and the forces which act on the plate to consist of (i.) a load which is a function of position distributed over the upper surface, and (ii.) a reaction on the under surface due to the base. Further, we assume the reaction of the base per unit area of the plate to be a function of the vertical displacement w of the element, and when account is taken of the small order of w this function can be taken to be linear in w .

On these assumptions we obtain a solution for the case of a symmetrically loaded circular plate in Section I., while in Section II. we work out an approximate solution for a rectangular plate loaded in any manner. We obtain the solution for the circular plate from the usual differential equation and boundary conditions, but in the case of the rectangular plate we use the method that Ritz developed in his paper on the deformation of a rectangular plate loaded at a point and clamped at the edges* and in that on the free vibrations of a rectangular plate†.

Section I.—*The Bending of a uniform thin flat circular Plate on a horizontal Base under a symmetrical Load.*

§ 1.

We use cylindrical coordinates (O, r, θ, z) such that Oz is vertically downwards and the origin O coincides with the centre of the middle section of the plate when there is no load. Then the equation‡ to determine the displacement w of an element in the direction of Oz is

$$\frac{1}{r} \frac{d}{dr} \left[r \frac{d}{dr} \left\{ \frac{1}{r} \frac{d}{dr} \left(r \frac{dw}{dr} \right) \right\} \right] = Z'/D, \quad \dots (1)$$

where Z' is the load per unit area of the plate, D the flexural rigidity

$$\frac{2Eh^3}{3(1-\sigma^2)},$$

E Young's modulus, σ Poisson's ratio, and $2h$ the thickness of the plate.

* Ritz, *Crelle*, cxxxv., cxxxvi. pp. 1-61 (1909).

† Ritz, *Annalen der Physik* (4te folge), xxviii. pp. 737-786 (1909).

‡ Love, 'Elasticity,' 4th ed., para. 314 (a), p. 489.

The bending-moment * about a tangent to a circle of radius r is

$$G_t = -D \left(\frac{d^2 w}{dr^2} + \frac{\sigma}{r} \frac{dw}{dr} \right),$$

and that about a radial line is

$$G_r = -\sigma D \frac{d^2 w}{dr^2},$$

while the torsional couples H are zero. The shearing stress along the boundary of a circle of radius r is

$$N_t = -D \left(\frac{d^3 w}{dr^3} + \frac{1}{r} \frac{d^2 w}{dr^2} - \frac{1}{r^2} \frac{dw}{dr} \right),$$

while that along a radial line is zero.

We assume that when loaded the plate and the foundation on which it rests always remain in contact and that the reaction on an element of the plate is a function of the displacement w of the element. Then, in view of the smallness of w , we may consider the reaction to be $(C + R w)$ per unit area, where C and R are constants. When the load on the upper surface of the plate is $f(r)$ per unit area, we obtain

$$Z' = f(r) - R w,$$

C being now included in $f(r)$. Of course, the weight of the plate may be regarded as part of the load, but it is usually negligible.

The equation (1) now becomes

$$\frac{d^4 w}{dr^4} + \frac{2}{r} \frac{d^3 w}{dr^3} - \frac{1}{r^2} \frac{d^2 w}{dr^2} + \frac{1}{r} \frac{dw}{dr} + \nu^4 w = f(r)/D, \quad (2)$$

where $\nu^4 = R/D$, a positive quantity. This equation may be written in the form

$$\left(\frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr} - i\nu^2 \right) \left(\frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr} + i\nu^2 \right) (w) = f(r)/D,$$

and then the complementary function can be written down in terms of Bessel functions with complex arguments †, while, of course, the particular integral depends on the form of $f(r)$.

* Love, *ibid.* para. 313, p. 488.

† Cf. Courant and Hilbert, 'Methoden der Math. Physik,' pp. 256-257.

For our purpose, the complementary function of (2) is best expressed by the series solutions of

$$\frac{d^4 w}{dr^4} + \frac{2}{r} \frac{d^3 w}{dr^3} - \frac{1}{r^2} \frac{d^2 w}{dr^2} + \frac{1}{r^3} \frac{dw}{dr} + \nu^4 w = 0.$$

Assuming the series

$$w(m, r) = \sum_{s=0}^{\infty} a_s r^{m+4s}, \quad (a_0 = 1),$$

the indicial equation is found to be

$$m^2(m-2)^2 = 0,$$

and so the complementary function of (2) is

$$C_1 \psi_1 + C_2 \psi_2 + C_3 \psi_3 + C_4 \psi_4,$$

where the C's are arbitrary constants, and

$$\psi_1 = [w(m, r)]_{m=0}, \quad \psi_2 = \left[\frac{\partial}{\partial m} \{w(m, r)\} \right]_{m=0},$$

$$\psi_3 = [w(m, r)]_{m=2}, \quad \psi_4 = \left[\frac{\partial}{\partial m} \{w(m, r)\} \right]_{m=2}.$$

The successive coefficients in $w(m, r)$ are connected by the relation

$$a_s(m+4s)^2(m+4s-2)^2 = -\nu^4 a_{s-1},$$

and so

$$w(m, r) = r^m [1 - b_1 \nu^4 r^4 + b_2 \nu^8 r^8 + \dots + (-1)^s b_s \nu^{4s} r^{4s} + \dots],$$

where

$$b_s = \frac{1}{(m+2)^2(m+4)^2 \dots (m+4s-2)^2(m+4s)^2}.$$

Also

$$\frac{\partial}{\partial m} [w(m, r)] = \left\{ w(m, r) \log r + r^m \sum_{s=1}^{\infty} \left[(-1)^s \frac{\partial b_s}{\partial m} \nu^{4s} r^{4s} \right] \right\},$$

and it is easily verified that

$$\frac{\partial b_s}{\partial m} = -2b_s \left[\frac{1}{m+2} + \frac{1}{m+4} + \dots + \frac{1}{m+4s} \right].$$

Hence we have

$$\psi_1 = 1 - \frac{\nu^4 r^4}{2^2 \cdot 4^2} + \frac{\nu^8 r^8}{2^2 \cdot 4^2 \cdot 6^2 \cdot 8^2} + \dots$$

$$+ (-1)^s \frac{\nu^{4s} r^{4s}}{2^2 \cdot 4^2 \cdot \dots (4s-2)^2 (4s)^2} + \dots,$$

$$\psi_2 = \psi_1 \log r + \sum_{s=1}^{\infty} [(-1)^{s+1} c_s \nu^{4s} r^{4s}],$$

where

$$c_s = \frac{2}{2^2 \cdot 4^2 \cdot \dots (4s-2)^2 (4s)^2} \left[\frac{1}{2} + \frac{1}{4} + \dots + \frac{1}{4s} \right],$$

$$\psi_3 = r^2 \left[1 - \frac{\nu^4 r^4}{4^2 \cdot 6^2} + \frac{\nu^8 r^8}{4^2 \cdot 6^2 \cdot 8^2 \cdot 10^2} + \dots \right.$$

$$\left. + (-1)^s \frac{\nu^{4s} r^{4s}}{4^2 \cdot 6^2 \cdot \dots (4s)^2 (4s+2)^2} + \dots \right],$$

$$\psi_4 = \psi_3 \log r + r^2 \sum_{s=1}^{\infty} [(-1)^{s+1} d_s \nu^{4s} r^{4s}],$$

where

$$d_s = \frac{2}{4^2 \cdot 6^2 \cdot \dots (4s)^2 (4s+2)^2} \left[\frac{1}{4} + \frac{1}{6} + \dots + \frac{1}{4s+2} \right].$$

There are no difficulties with the convergence of the ψ 's and their differential coefficients, and in all cases the convergence is rapid.

§ 2.

We now consider the case of a circular plate of radius r_2 on which the loading is uniform over a circle of radius r_1 ($r_1 < r_2$). Let p_0 be the constant load per unit area. Then the complete solution of (2), which holds inside the circle of radius r_1 , is

$$w_1 = \frac{p_0}{R} + E_1 \psi_1 + E_3 \psi_3, \quad (E\text{'s constant})$$

since w must be finite at the origin. The solution over the remainder of the plate is

$$w_2 = F_1 \psi_1 + F_2 \psi_2 + F_3 \psi_3 + F_4 \psi_4, \quad (F\text{'s constant}).$$

On the boundary of the circle of radius r_1 , w and $\frac{dw}{dr}$ must

be continuous, and likewise the bending-moment and shearing-stress, and so at this boundary $\frac{d^2w}{dr^2}$ and $\frac{d^3w}{dr^3}$ must also be continuous. Further, at the outer boundary of the plate the bending-moment G_t and the shearing-stress N_t must be zero. These conditions are expressed by the following six equations :—

$$\begin{aligned} \left[\frac{p_0}{R} + E_1\psi_1 + E_3\psi_3 \right]_{r=r_1} &= \left[F_1\psi_1 + F_2\psi_2 + F_3\psi_3 + F_4\psi_4 \right]_{r=r_1}, \\ \left[E_1 \frac{d^n\psi_1}{dr^n} + E_3 \frac{d^n\psi_3}{dr^n} \right]_{r=r_1} &= \left[F_1 \frac{d^n\psi_1}{dr^n} + F_2 \frac{d^n\psi_2}{dr^n} + F_3 \frac{d^n\psi_3}{dr^n} + F_4 \frac{d^n\psi_4}{dr^n} \right]_{r=r_1}, \\ &\quad (n=1, 2, 3), \end{aligned}$$

$$\begin{aligned} \left[\sum_{q=1}^4 \left\{ F_q \left(\frac{d^2\psi_q}{dr^2} + \frac{\sigma}{r} \frac{d\psi_q}{dr} \right) \right\} \right]_{r=r_2} &= 0, \\ \left[\sum_{q=1}^4 \left\{ F_q \left(\frac{d^3\psi_q}{dr^3} + \frac{1}{r} \frac{d^2\psi_q}{dr^2} - \frac{1}{r^2} \frac{d\psi_q}{dr} \right) \right\} \right]_{r=r_2} &= 0, \end{aligned}$$

which determine the values of the constants E and F completely.

Section II.—*The Bending of a uniform thin flat rectangular Plate on a horizontal Base under a prescribed Load.*

§ 1.

We use a rectangular system of Cartesian coordinates (O, x , y , z), such that Oz is vertically downwards and the plane xOy coincides with the middle plane of the plate when there is no load. Denoting the displacement in the direction of Oz by w when the plate is strained, the potential energy * of the plate due to internal elastic effects is

$$\begin{aligned} \frac{1}{2}D \iint \left[\left(\frac{\partial^2 w}{\partial x^2} \right)^2 + \left(\frac{\partial^2 w}{\partial y^2} \right)^2 + 2\sigma \frac{\partial^2 w}{\partial x^2} \cdot \frac{\partial^2 w}{\partial y^2} \right. \\ \left. + 2(1-\sigma) \left(\frac{\partial^2 w}{\partial x \partial y} \right)^2 \right] dx dy, \end{aligned}$$

* Rayleigh, 'Sound,' i. 2nd ed. (1926) p. 353.

taken over the surface of the plate, D etc. having the same meanings as in Section I.

As before, we may consider the reaction of the base to be $(C + R w)$ per unit area, where C and R are constants. When the load on the plate is $f(x, y)$ per unit area, we find the extraneous force in the direction of Oz to be

$$[f(x, y) - R w] \text{ per unit area,}$$

where C is now included in $f(x, y)$.

The work done by this extraneous force on an element of unit area in a displacement δw is

$$[f(x, y) - R w] \delta w = \delta [f(x, y) w - \frac{1}{2} R w^2],$$

and so when the plate is loaded the work done by this agency is

$$\iint [f(x, y) w - \frac{1}{2} R w^2] dx dy,$$

taken over the surface of the plate.

Combining these results we find the total energy of the loaded plate to be

$$V = \iint \left\{ \frac{1}{2} D \left[\left(\frac{\partial^2 w}{\partial x^2} \right)^2 + \left(\frac{\partial^2 w}{\partial y^2} \right)^2 + 2\sigma \frac{\partial^2 w}{\partial x^2} \cdot \frac{\partial^2 w}{\partial y^2} + 2(1 - \sigma) \left(\frac{\partial^2 w}{\partial x \partial y} \right)^2 \right] - [f(x, y) w - \frac{1}{2} R w^2] \right\} dx dy. \quad (3)$$

The Ritz process consists in assuming for w a double series of suitably chosen orthogonal functions ψ_m ,

$$w' = \sum_{m=0}^r \sum_{n=0}^s A_{mn} \psi_m(x) \psi_n(y),$$

and substituting w' for w in (3). Denoting by V' the form that (3) then assumes, we see that V' is a quadratic function of the coefficients A_{mn} and that its stationary value is determined by the equations

$$\frac{\partial V'}{\partial A_{mn}} = 0,$$

which are linear in the A_{mn} 's. When the values of A_{mn} which satisfy these equations are put in w' a double series is obtained whose limiting form, when r and s tend to infinity, is the solution of the problem. In the practical case w' gives an approximate solution.

§ 2.

We now examine the rectangular plate bounded by

$$x = \pm a, \quad y = \pm b.$$

The system of orthogonal functions which we use are those that Ritz * employed in his investigation of the free vibrations of a rectangular plate. These functions arise in determining the transverse vibrations of a free uniform straight rod, and are different solutions of the equation

$$\frac{d^4 u}{d\xi^4} = k_m u.$$

The forms chosen are :

$$\left. \begin{aligned} u_0(\xi) &= 1/\sqrt{2}, \\ u_m(\xi) &= \frac{\cosh k_m \cos k_m \xi + \cos k_m \cosh k_m \xi}{\sqrt{(\cosh^2 k_m + \cos^2 k_m)}}, \\ \text{where } \tan k_m + \tanh k_m &= 0, \end{aligned} \right\} \quad (m \text{ even}),$$

and

$$\left. \begin{aligned} u_1(\xi) &= \xi\sqrt{3}/\sqrt{2}, \\ u_m(\xi) &= \frac{\sinh k_m \sin k_m \xi + \sin k_m \sinh k_m \xi}{\sqrt{(\sinh^2 k_m - \sin^2 k_m)}}, \\ \text{where } \tan k_m - \tanh k_m &= 0. \end{aligned} \right\} \quad (m \text{ odd}),$$

The values of k_m are approximately

$$k_0 = 0, \quad k_1 = 0, \quad k_2 = 2.3650, \quad k_3 = 3.9266,$$

$$k_4 = 7\pi/4, \dots \quad k_m = (m - \frac{1}{2})\frac{\pi}{2}, \dots$$

These functions are even or odd according as m is even or odd, and form a complete orthogonal system such that

$$\int_{-1}^{+1} u_m(\xi) u_n(\xi) d\xi = 0, \quad (m \neq n),$$

$$\int_{-1}^{+1} u_m^2(\xi) d\xi = 1,$$

In addition, they are so chosen that $\frac{d^2 u_m}{d\xi^2}$ and $\frac{d^3 u_m}{d\xi^3}$ vanish

* Ritz, *Annalen der Physik*, l. c.

at $\xi = \pm 1$, and this is done in order to facilitate the evaluation of the integrals which arise.

As

$$u_m'(\xi) = k_m \frac{[-\cosh k_m \sin k_m \xi + \cos k_m \sinh k_m \xi]}{\sqrt{(\cosh^2 k_m + \cos^2 k_m)}}, \quad (m \text{ even}),$$

etc.,

in our subsequent work we always write

$$u_m'(x/a) = k_m \frac{[-\cosh k_m \sin(k_m x/a) + \cos k_m \sinh(k_m x/a)]}{\sqrt{(\cosh^2 k_m + \cos^2 k_m)}},$$

etc. (m even),

We may also note that for all values of m and n ,

$$\int_{-a}^a u_m(x/a) u_n(x/a) dx = 0, \quad (m \neq n),$$

$$\int_{-a}^a u_m^2(x/a) dx = a.$$

§ 3.

When we take the form

$$w_1 = \sum_{m=0}^s \sum_{n=0}^s A_{mn} u_m(x/a) u_n(y/b),$$

and carry out the above process, we obtain the equations

$$\frac{\partial J_2}{\partial A_{mn}} = \frac{\partial J_1}{\partial A_{mn}}, \quad (m, n = 0, 1, 2, \dots, s);$$

where

$$J_1 = \frac{2}{D} \int_{-a}^a \int_{-b}^b w_1 f(x, y) dx dy,$$

$$J_2 = \int_{-a}^a \int_{-b}^b \left[\left(\frac{\partial^2 w_1}{\partial x^2} \right)^2 + \left(\frac{\partial^2 w_1}{\partial y^2} \right)^2 + 2\sigma \frac{\partial^2 w_1}{\partial x^2} \cdot \frac{\partial^2 w_1}{\partial y^2} \right. \\ \left. + 2(1-\sigma) \left(\frac{\partial^2 w_1}{\partial x \partial y} \right)^2 + \lambda w_1^2 \right] dx dy,$$

and

$$\lambda = R/D.$$

J_1 is a linear function of the A_{mn} 's, which we write in the form

$$J_1 = 2 \sum_{m=0}^s \sum_{n=0}^s \delta_{mn} A_{mn},$$

$$\begin{aligned}
& + \frac{2(1-\sigma)}{a^2 b^2} \int_{-a}^a \int_{-b}^b [u_m'(x/a)]^2 [u_n'(y/b)]^2 dx dy \\
& + \lambda \int_{-a}^a \int_{-b}^b [u_m(x/a)]^2 [u_n(y/b)]^2 dx dy \\
& = \frac{b}{a^3} \beta_{mm} + \frac{a}{b^3} \beta_{nn} + \frac{2\sigma}{ab} \omega_{mm} \omega_{nn} + \frac{2(1-\sigma)}{ab} \alpha_{mm} \alpha_{nn} + \lambda ab;
\end{aligned}$$

(ii.) when m, n are not identical with p, q respectively,

$$\begin{aligned}
\gamma_{mn, pq} &= \frac{1}{a^4} \int_{-a}^a \int_{-b}^b u_m''(x/a) u_p''(x/a) u_n(y/b) u_q(y/b) dx dy \\
& + \frac{1}{b^4} \int_{-a}^a \int_{-b}^b u_m(x/a) u_p(x/a) u_n''(y/b) u_q''(y/b) dx dy \\
& + \frac{\sigma}{a^2 b^2} \int_{-a}^a \int_{-b}^b u_m''(x/a) u_p(x/a) \\
& \quad \times u_n(y/b) u_q''(y/b) dx dy \\
& + \frac{\sigma}{a^2 b^2} \int_{-a}^a \int_{-b}^b u_p''(x/a) u_m(x/a) \\
& \quad \times u_n''(y/b) u_q(y/b) dx dy \\
& + \frac{2(1-\sigma)}{a^2 b^2} \int_{-a}^a \int_{-b}^b u_m'(x/a) u_p'(x/a) \\
& \quad \times u_n'(y/b) u_q'(y/b) dx dy \\
& + \lambda \int_{-a}^a \int_{-b}^b u_m(x/a) u_p(x/a) u_n(y/b) u_q(y/b) dx dy \\
& = \frac{b}{a^3} \beta_{mp} \int_{-1}^1 u_n(\xi) u_q(\xi) d\xi + \frac{a}{b^3} \beta_{nq} \int_{-1}^1 u_m(\xi) u_p(\xi) d\xi \\
& + \frac{\sigma}{ab} (\omega_{mp} \omega_{qn} + \omega_{pm} \omega_{nq}) + \frac{2(1-\sigma)}{ab} \alpha_{mp} \alpha_{nq}.
\end{aligned}$$

In the above formulæ

$$\begin{aligned}
\alpha_{mn} &= \alpha_{nm} = \int_{-1}^1 u_m'(\xi) u_n'(\xi) d\xi, \\
\beta_{mn} &= \beta_{nm} = \int_{-1}^1 u_m''(\xi) u_n''(\xi) d\xi, \\
\omega_{mn} &= \int_{-1}^1 u_m''(\xi) u_n(\xi) d\xi.
\end{aligned}$$

The values of these integrals are :

$$\alpha_{nn} = \alpha_{0n} = 0,$$

$$\alpha_{1n} = 0 \quad (n \text{ even})$$

$$= 2\sqrt{\left(\frac{3}{2}\right)} \cdot u_n(1) \quad (n \text{ odd}),$$

$$\alpha_{mn} = 0 \quad \left\{ \begin{array}{l} m \text{ even and } n \text{ odd} \\ \text{or } m \text{ odd and } n \text{ even} \end{array} \right\}$$

$$= 2 \frac{k_m^4 u_m(1) u_n'(1) - k_n^4 u_m'(1) u_n(1)}{k_m^4 - k_n^4}$$

(m and n both even or both odd),

$$\alpha_{mn} = \frac{k_m^2 (\cosh^2 k_m - \cos^2 k_n) + 6k_m \cos^2 k_m \sinh k_m \cosh k_m}{\cosh^2 k_m + \cos^2 k_m} \quad (m \text{ even})$$

$$= \frac{k_m^2 (\sinh^2 k_m + \sin^2 k_n) + 6k_m \sin^2 k_m \sinh k_m \cosh k_m}{\sinh^2 k_m - \sin^2 k_m} \quad (m \text{ odd}),$$

$$\beta_{nn} = 0 \quad (m \neq n),$$

$$\beta_{mn} = k_n^4,$$

$$\omega_{0n} = \omega_{1n} = 0,$$

$$\omega_{m0} = \sqrt{2} \cdot k_m \frac{(-\cosh k_m \sin k_m + \cos k_n \sinh k_m)}{\sqrt{(\cosh^2 k_m + \cos^2 k_m)}} \quad (m \text{ even})$$

$$= 0 \quad (m \text{ odd}),$$

$$\omega_{mn} = 0 \quad \left\{ \begin{array}{l} m \text{ even and } n \text{ odd} \\ \text{or } m \text{ odd and } n \text{ even} \end{array} \right\}$$

$$= 2k_m^4 \cdot \frac{u_m'(1) u_n(1) - u_m(1) u_n'(1)}{k_m^4 - k_n^4}$$

(m and n both even or both odd, $m \neq n$).

$$\omega_{mn} = \frac{-k_m^2 (\cosh^2 k_m - \cos^2 k_n) + 2k_m \cos^2 k_m \sinh k_m \cosh k_m}{\cosh^2 k_m + \cos^2 k_m} \quad (m \text{ even})$$

$$= \frac{-k_m^2 (\sinh^2 k_m + \sin^2 k_n) + 2k_m \sin^2 k_m \sinh k_m \cosh k_m}{\sinh^2 k_m - \sin^2 k_m} \quad (m \text{ odd}).$$

Taking these data into consideration we finally obtain

$$\gamma_{mn, mn} = \frac{b}{a^3} k_m^4 + \frac{a}{b^3} k_n^4 + \frac{2\sigma}{ab} \omega_{mm} \omega_{nn} + \frac{2(1-\sigma)}{ab} \alpha_{mn} \alpha_{nn} + \lambda ab$$

and . . . (5)

$$\gamma_{mn, pq} = \frac{\sigma}{ab} (\omega_{mp} \omega_{qn} + \omega_{pm} \omega_{nq}) + \frac{2(1-\sigma)}{ab} \alpha_{mp} \alpha_{nq} . . . (6)$$

when p, q are not respectively equal to m, n .

Further, it readily follows that

(i.) $\gamma_{mn, pq} = \gamma_{pq, mn} = \gamma_{nm, qp} = \gamma_{qp, nm}$;

(ii.) if any three of m, n, p, q are zero,

$$\gamma_{mn, pq} = 0 ;$$

(iii.) if $m \neq 0, n \neq 0$,

$$\gamma_{00, mn} = 0 ;$$

(iv.) if $m \neq 0, n \neq 0$, and $m \neq n$,

$$\gamma_{m0, n0} = 0 ;$$

(v.) if $m \neq 0, n \neq 0$,

$$\gamma_{m0, 0n} = \frac{\sigma}{ab} \omega_{m0} \omega_{n0} ;$$

(vi.) if only one of m, n, p, q is zero,

$$\gamma_{mn, pq} = \frac{\sigma}{ab} (\omega_{mp} \omega_{qn} + \omega_{pm} \omega_{nq}).$$

When m is greater than 3 the values of k_m differ from $(m - \frac{1}{2}) \frac{\pi}{2}$ by a very small quantity, and so we can write down the following close approximations which facilitate the evaluation of the coefficients of the equations (4).

When $m > 3, n > 3$, these formulæ are :

$$u_m(\xi) = \cos(m - \frac{1}{2}) \frac{\pi \xi}{2} + (-1)^{m/2} \frac{\cosh(m - \frac{1}{2}) \frac{\pi \xi}{2}}{\sqrt{2} \cdot \cosh(m - \frac{1}{2}) \frac{\pi}{2}} \quad (m \text{ even})$$

$$= \sin(m - \frac{1}{2}) \frac{\pi \xi}{2} + (-1)^{(m-1)/2} \frac{\sinh(m - \frac{1}{2}) \frac{\pi \xi}{2}}{\sqrt{2} \cdot \sinh(m - \frac{1}{2}) \frac{\pi}{2}} \quad (m \text{ odd}),$$

which satisfy the equations approximately, and then a closer approximation will be given by

$$(A'_{01} + \epsilon_{01}), (A'_{10} + \epsilon_{10}), \dots, (A'_{mn} + \epsilon_{mn}), \dots, (A'_{ss} + \epsilon_{ss}).$$

On account of the relative magnitude of the coefficients the equation to determine ϵ_{mn} is

$$\gamma_{mn, mn} \epsilon_{mn} = \delta_{mn} - [\gamma_{01, mn} A'_{01} + \gamma_{10, mn} A'_{10} + \dots + \gamma_{mn, mn} A'_{mn} + \dots + \gamma_{ss, mn} A'_{ss}].$$

In practice, the method adopted is to solve

$$\left. \begin{aligned} \gamma_{01, 01} A_{01} + \gamma_{10, 01} A_{10} + \gamma_{11, 01} A_{11} &= \delta_{01}, \\ \gamma_{01, 10} A_{01} + \gamma_{10, 10} A_{10} + \gamma_{11, 10} A_{11} &= \delta_{10}, \\ \gamma_{01, 11} A_{01} + \gamma_{10, 11} A_{10} + \gamma_{11, 11} A_{11} &= \delta_{11}, \end{aligned} \right\}$$

in the first place. If the values satisfying these equations are B_{01} , B_{10} , B_{11} , say, we get approximations for the next two A 's, say B_{02} and B_{20} , from

$$\gamma_{01,02} \mathbf{B}_{01} + \gamma_{10,02} \mathbf{B}_{10} + \gamma_{11,02} \mathbf{B}_{11} + \gamma_{02,02} \mathbf{B}_{02} = \delta_{02},$$

$$\gamma_{01,20}B_{01}+\gamma_{10,20}B_{10}+\gamma_{11,20}B_{11}+\gamma_{20,20}B_{20}=\delta_{20}.$$

We then use these values $B_{01}, B_{10}, B_{11}, B_{02}, B_{20}$ as first approximations to the solution of the five equations,

[illegible]

and determine the necessary corrections, ϵ_{01} , etc., to these values in accordance with the above plan.

This process becomes prohibitive if it is required to get more than the first eight or nine A's. However, in the cases examined the first eight or nine terms of w_1 , with the coefficients so obtained, give quite a satisfactory approximate solution of the problem.

PART II.

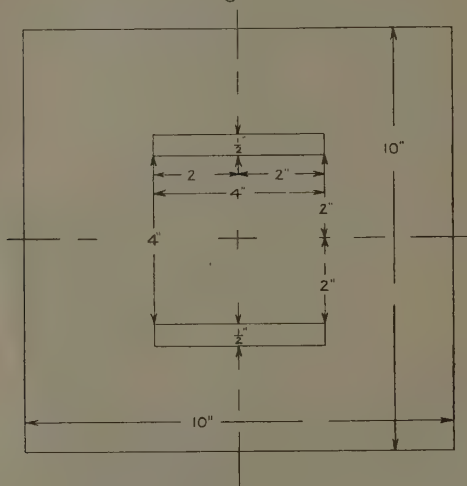
§ 1.

In devising an experiment to check the problem investigated in Part I. our major difficulty was the determination of the constant λ . After various attempts with different media we decided, on the advice of Professor A. J. S.

Pippard, to support a plate on a set of springs as illustrated in Pl. I. fig. 1.

In this report we do not deem it necessary to include the results of all our experiments, and so we only give as a typical example the case for a rectangular mild steel plate, 10 in. square and $\cdot 2345$ in. thick, machined on all surfaces and edges, and scribed into squares on the upper face by parallels to the edges at intervals of 1 in. This plate was supported on 81 springs of 1 in. external diameter symmetrically located under the entire lower

Fig. 1.



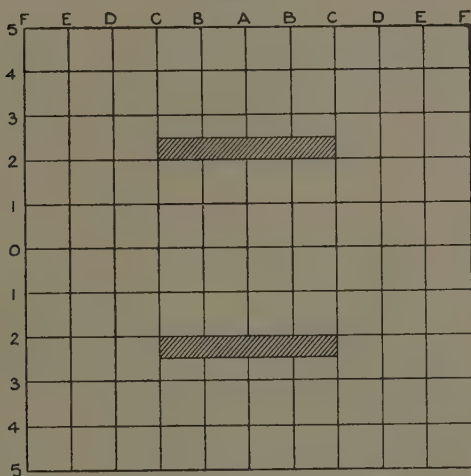
Showing position of stool on plate.

surface of the plate (*cf.* Pl. I. fig. 2). The above apparatus was set up on the floating table of a compression-testing machine *. As observations showed that the load transmitted by a rolled steel joist acting as a stanchion is communicated to the plate by the outer edges of the flanges only, the steel stool to be seen in Pl. I. fig. 2 was constructed for the purpose. The cross-sectional dimensions of the two upright plates of the stool are 4 in. by $\cdot 5$ in., and these are dapped into the top

* The machine used was electrically operated and of the vertical single lever type with a screw ram.

cross-plate with an inside clearance of 4 in. The stool was placed symmetrically on the plate, as indicated in fig. 1, and the load was communicated to the stool from the machine through a hardened steel ball placed vertically over the centre of the plate. As the springs had a linear deflexion-load curve it was found convenient to take the difference of the deflexions at the several points for loads of $\frac{1}{2}$ ton and $1\frac{1}{2}$ tons. This method ensured that the plate was bearing properly on the springs and so gave the deflexions per ton load. The measurement of the deflexions

Fig. 2.



Showing reference points on plate.

was directly made on the plate with Ames dials, reading to ten thousandths of an inch and rigidly supported. The readings were taken for the points specified in fig. 2, and to minimize experimental errors the mean deflexions at these points are given for the four quadrants of the plate and are to be found in Table I.

§ 2.

To obtain the numerically approximate solution for the case dealt with in § 1, Part II., by the method of § 5, Part I., it was necessary to get the elastic constants of

the plate and the springs, and the approximate areas of contact of the stool with the plate. The elastic constants of the plate used were $E=13,050$ tons per sq. in. and

TABLE I.

Showing actual Mean and Calculated Deflexions in inches for One Quadrant of the Plate, together with Percentage Differences.

	A.	B.	C.	D.	E.	F.
0. { Experimental	·14403	·14281	·14048	·13586	·13149	·12701
{ Calculated ...	·14568	·14494	·14266	·13883	·13482	·12833
{ Percent. diff.	-1·13	-1·47	-1·522	-2·13	-2·47	-1·02
1. { Experimental	·14266	·14190	·14060	·13707	·13449	·12738
{ Calculated ...	·14531	·14459	·14226	·13850	·13344	·12787
{ Percent. diff.	-1·82	-1·86	-1·17	-1·03	-1·46	-0·38
2. { Experimental	—	—	—	·13688	·13122	·12646
{ Calculated ...	·14396	·14333	·14096	·13743	·13241	·12685
{ Percent. diff.	—	—	—	-0·465	-0·9	-0·308
3. { Experimental	—	—	—	·13498	·13030	·12530
{ Calculated ...	·14163	·14096	·13880	·13503	·12995	·12430
{ Percent. diff.	—	—	—	-0·034	+0·27	+0·805
4. { Experimental	·13893	·13840	·13809	·13286	·12783	·12285
{ Calculated ...	·13802	·13730	·13514	·13147	·12648	·12102
{ Percent. diff.	+0·667	+0·845	+2·13	+1·056	+1·067	+1·51
5. { Experimental	·13645	·13816	·13410	·13033	·12553	·12130
{ Calculated ...	·13381	·13308	·13090	·12737	·12258	·11746
{ Percent. diff.	+1·97	+3·82	+2·44	+2·32	+2·41	+3·23

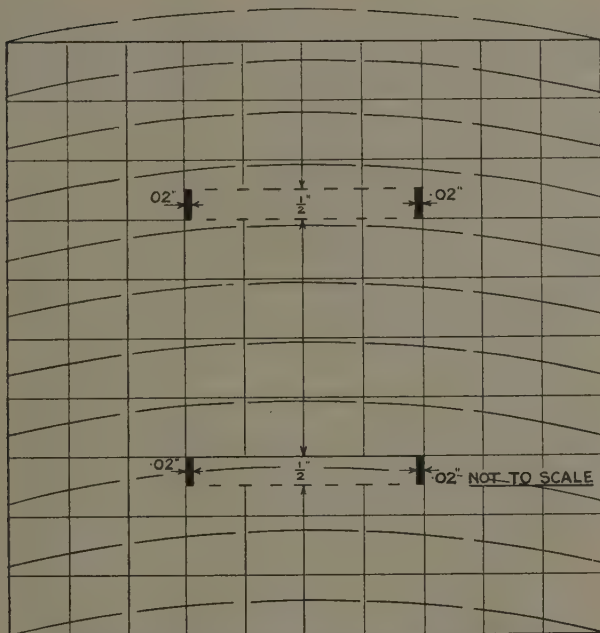
$\sigma=0\cdot2755$, and the elastic constant of the springs gave a value of $\lambda a^2=0\cdot1213085$ in the notation of § 2, Part I.

The portion of the stool in contact with the plate was estimated to be a rectangular strip $\cdot5 \times \cdot02$ in. (*cf.* fig. 3) at each corner, as yielding was observed at the outer edges of these areas and the plate was cambered under the sides of the stool. The total load was then assumed to be uniformly distributed over these four small areas.

The constants $\gamma_{mn, pq}$ required for the solution of (7) were calculated from (5) and (6) and the other results of § 4, Part I., while the δ_{rs} 's were calculated directly. The process sketched in § 5, Part I., was then used to obtain the approximate values of

$$A_{00}, A_{02}, A_{20}, A_{22}, A_{04}, A_{40}, A_{24}, A_{42}, \text{ and } A_{44}.$$

Fig. 3.



Showing areas of contact of stool and deflexion contours.

Note.—Value of deflexion F5 has been subtracted from all deflexions.

Finally, the corresponding approximations for

$$w_1 = \frac{1}{a^2} \sum_{m=0}^2 \sum_{n=0}^2 A_{2m, 2n} u_{2m}(x/a) u_{2n}(y/b)$$

were calculated for each reference point by means of double entry tables. These results are given in Table I. The percentage errors between experimental and calculated

values of w are to be found in this table and are within the range of experimental error.

TABLE II.

Showing Calculated Deflexions in inches for One Quadrant of the Plate with uniform upward Pressure.

	A.	B.	C.	D.	E.	F.
0	·010739	·009909	·007376	·003197	—·002208	—·008083
1	·010357	·009545	·007044	·002869	—·002603	—·008565
2	·009000	·008235	·006078	·001602	—·003954	—·010052
3	·006347	·005583	·003177	·000140	—·006473	—·011838
4	·002519	·001732	—·000691	—·004732	—·010024	—·015789
5	—·001848	—·002671	—·005144	—·009080	—·014030	—·019345

TABLE III.

Showing Deflexions of Table II. increased by 0·134942 in. together with Percentage Differences from Deflexions of Table I.

	A.	B.	C.	D.	E.	F.
0	{ ·145681 —	{ ·144851 —	{ ·142318 —	{ ·138139 $\frac{1}{2}$	{ ·132734 $1\frac{1}{2}$	{ ·126859 $1\frac{1}{2}$
1	{ ·145299 —	{ ·144487 —	{ ·141986 —	{ ·137811 $\frac{1}{2}$	{ ·132339 1	{ ·126377 1
2	{ ·143942 —	{ ·143177 —	{ ·141020 —	{ ·136544 1	{ ·130988 1	{ ·124890 1
3	{ ·141289 —	{ ·140525 —	{ ·138119 —	{ ·135082 —	{ ·128469 1	{ ·123404 1
4	{ ·137461 $\frac{1}{2}$	{ ·136674 $\frac{1}{2}$	{ ·134251 1	{ ·130210 1	{ ·124918 1	{ ·119153 $1\frac{1}{2}$
5	{ ·133094 $\frac{1}{2}$	{ ·132271 $\frac{1}{2}$	{ ·129798 1	{ ·125862 $1\frac{1}{2}$	{ ·120912 $1\frac{1}{2}$	{ ·115597 2

Fig. 3 gives the deflexion contours arising from the calculation.

In view of the general rule of practice that the reaction between the bed and the plate is one of uniform pressure, we calculated the deflexions for the same plate under the same load when the upward pressure is taken to be uniform. In this case the reaction contributes to the δ_{rs} 's while λ is zero. The deflexions thus calculated are given in Table II. By adding .134942 in. to all the numbers in Table II. and then taking the differences with the corresponding numbers in Table I., we are able to get some idea of the relative curvatures of the plate in the two cases. These are given in Table III., together with the percentage differences based on those of Table I. So the assumption of the uniform reaction does not imply any marked alterations in the curvature of the plate, and consequently there is no marked divergence between the stresses and bending-moments depending on either assumption. The numerical values of the stresses and bending-moments in these cases have been obtained for a few selected reference points and show no marked variation.

Our thanks are due to Professor Andrew Robertson, Dean of the Faculty of Engineering, and to Professor A. J. Sutton Pippard for permission to carry out the experimental work in the testing laboratory of the department of Civil Engineering in the University of Bristol, and for their advice and assistance on numerous occasions.

We also wish to acknowledge the valuable assistance rendered by Mr. R. R. Holder in the computation and experimental work.

II. *The Temperature Field in an Air Current flowing across a Hot Cylinder.* By JAMES SMALL, B.Sc., Ph.D., Carnegie Teaching Fellow, The University of Glasgow*.

LET MM'N'N in fig. 1 represent an element of the fluid flowing past a hot plane surface AB with velocity V. It will be assumed that the fluid is non-viscous and incompressible, and that the effects of temperature on its density and on its volumetric heat capacity are

* Communicated by the Author.

negligible. The equation governing the distribution of temperature in the fluid is

$$\nabla_{xy}^2 \theta = \frac{cV}{K} \cdot \frac{\partial \theta}{\partial x}, \quad \dots \dots \dots (i.)$$

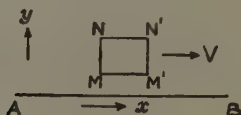
where c is the heat capacity of the fluid per unit volume at constant pressure, V is its velocity, and K its coefficient of thermal conduction.

When the term $\frac{\partial^2 \theta}{\partial x^2}$ is neglected, as is general in this type of problem, the equation may be written *

$$\frac{\partial \theta}{\partial x} = \frac{K}{cV} \cdot \frac{\partial^2 \theta}{\partial y^2} \quad \dots \dots \dots (ii.)$$

Now take the case of a semi-infinite rod, with its axis parallel to the y -axis, to which at time $t=0$ a temperature

Fig. 1.



T is applied at $y=0$. The temperature θ at y conforms to the equation

$$\frac{\partial \theta}{\partial t} = \frac{K}{c} \cdot \frac{\partial^2 \theta}{\partial y^2} \quad \dots \dots \dots (iii.)$$

The solution † of this is

$$\theta = T \left(1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{y}{2\sqrt{\frac{K}{c} \cdot t}}} e^{-\xi^2} d\xi \right) \quad \dots \dots (iv.)$$

Suppose the rod to move in the x -direction with velocity V (fig. 2), and that at time $t=0$ its end $y=0$ makes contact with the hot plane, temperature T , at A . Since $V=x/t$, the equation (iii.) may be written

$$\frac{\partial \theta}{\partial x} = \frac{K}{cV} \cdot \frac{\partial^2 \theta}{\partial y^2}$$

* cf. Russell, Phil. Mag. xx. p. 591 (1910).

† Vide Carslaw's 'Conduction of Heat.'

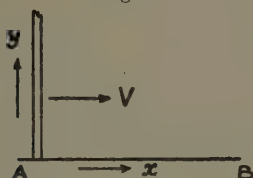
This is identical with equation (ii.), and the rod may therefore be regarded as an element of the fluid, and the solution becomes

$$\theta = T \left(1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{y}{2\sqrt{\frac{K}{cV} \cdot x}}} e^{-\xi^2} d\xi \right) \quad \dots \quad (v.)$$

Values of the integral for different values of ξ are tabulated in de Morgan's 'Essay on Probabilities' (1838) and in a paper by Burgess in the 'Transactions of the Royal Society of Edinburgh,' no. 39, 1899. It is possible, therefore, to construct the isotherms in the fluid between the perpendiculars through A and B. For, if equation (iv.) is written

$$1 - \frac{\theta}{T} = \Phi \left(\frac{y}{2\sqrt{\frac{K}{cV} \cdot x}} \right) = H,$$

Fig. 2.



and if values are chosen for θ/T , then the values of H can be written down. The corresponding figures for

$$\frac{y}{2\sqrt{\frac{K}{cV} \cdot x}} = S$$

are read from the tables, and since

$$y = 2S \sqrt{\frac{K}{cV} \cdot x}$$

for a given value of θ/T , the isotherms in the region dealt with are parabolic.

For the sake of having the isotherms widely enough spaced for graphical representation, a value of cV/K fictitiously small is chosen, in this case $\frac{1}{4}$. Hence

$$y = 4S\sqrt{x}.$$

Regarding the plane as of 32 units in length, the y -values for given values of θ/T are set forth in Table I.

In the region to the right of B the elementary rod of fluid is now no longer in contact with the surface; but the distribution of temperature along the rod as it passes out of contact with the plane at B is known. It is found to conform closely to $\theta = e^{-ay-by^2}$.

Making use of the symmetry of the field above and below the plane, and now assuming $t=0$ and $x=0$ at B, the temperature θ at any later instant of time and at any distance y along the now infinite rod may be regarded as due to an infinite number of plane sources (conforming

TABLE I.

$\frac{\theta}{T}$	H.	S.	\bar{w}_1							
			4.	8.	12.	16.	20.	24.	28.	32.
			$4S\sqrt{x}$							
0.9	0.1	0.089	0.712	1.002	1.23	1.42	1.59	1.74	1.89	2.05
0.8	0.2	0.179	1.432	2.015	2.38	2.86	3.20	3.51	3.79	4.05
0.7	0.3	0.273	2.178	3.07	3.78	4.36	4.87	5.34	5.77	6.16
0.6	0.4	0.371	2.968	4.19	5.15	5.94	6.64	7.27	7.86	8.40
0.5	0.5	0.477	3.816	5.37	6.62	7.64	8.54	9.35	10.10	10.79
0.4	0.6	0.595	4.760	6.71	8.25	9.52	10.63	11.66	12.60	13.46
0.3	0.7	0.733	5.864	8.54	10.15	11.71	13.10	14.36	15.50	16.59
0.2	0.8	0.907	7.256	10.20	12.56	14.51	16.20	17.78	19.20	20.52
0.1	0.9	1.163	9.304	13.10	16.13	18.61	20.80	22.80	24.62	26.32

to $\theta=f(y')$ say) applied at time $t=0$. Since $t=x/V$, we have

$$\theta = \int_{-\infty}^{\infty} \frac{f(y') e^{-\frac{(y-y')^2}{4\frac{Kx}{cV}}}}{2\sqrt{\pi\frac{Kx}{cV}}} dy' \dots \dots \dots \text{(vi.)}$$

Making the substitutions for $f(y')$ and cV/K in equation (vi.), it becomes

$$\theta = \int_{-\infty}^0 \frac{e^{ay'-by'^2-\frac{(y-y')^2}{16x}}}{4\sqrt{\pi x}} dy' + \int_0^{\infty} \frac{e^{-ay'-by'^2-\frac{(y-y')^2}{16x}}}{4\sqrt{\pi x}} dy'.$$

But

$$\begin{aligned}
 ay' - by'^2 - \frac{(y-y')^2}{16x} &= -\left(b + \frac{1}{16x}\right) \left(y' - \frac{a + \frac{y}{8x}}{2\left(b + \frac{1}{16x}\right)}\right)^2 \\
 &\quad + \frac{\left(a + \frac{y}{8x}\right)^2}{4\left(b + \frac{1}{16x}\right)} - \frac{y'^2}{16x} \\
 &= -A(y' - B_1)^2 + C_1 - D.
 \end{aligned}$$

Similarly,

$$-ay' - by'^2 - \frac{(y-y')^2}{16x} = -A(y' + B_2)^2 + C_2 - D,$$

where

$$B_2 = \frac{a - \frac{y}{8x}}{2\left(b - \frac{1}{16x}\right)} \quad \text{and} \quad C_2 = \frac{\left(a - \frac{y}{8x}\right)^2}{4\left(b - \frac{1}{16x}\right)};$$

therefore

$$\begin{aligned}
 \theta &= \frac{1}{4\sqrt{\pi x}} \left[\int_{-\infty}^0 e^{-A(y' - B_1)^2 + C_1 - D} dy' + \int_0^{\infty} e^{-A(y' + B_2)^2 + C_2 - D} dy' \right] \\
 &= \frac{1}{4\sqrt{\pi x}} [e^{C_1 - D} I_1 + e^{C_2 - D} I_2], \\
 I_1 &= \int_{-\infty}^0 e^{-A(y' - B_1)^2} dy' = \frac{1}{\sqrt{A}} \int_{-\infty}^{-B_1\sqrt{A}} e^{-z_1^2} dz_1,
 \end{aligned}$$

where

$$z_1 = \sqrt{A}(y' - B_1);$$

therefore

$$\begin{aligned}
 I_1 &= \frac{1}{\sqrt{A}} \int_0^{\infty} e^{-z_1^2} dz_1 - \frac{1}{\sqrt{A}} \int_0^{B_1\sqrt{A}} e^{-z_1^2} dz_1 \\
 &= \frac{1}{\sqrt{A}} \left(\frac{\sqrt{\pi}}{2} - \int_0^{B_1\sqrt{A}} e^{-z_1^2} dz_1 \right).
 \end{aligned}$$

Similarly,

$$I_2 = \frac{1}{\sqrt{A}} \left(\frac{\sqrt{\pi}}{2} - \int_0^{B_2\sqrt{A}} e^{-z_2^2} dz_2 \right).$$

B_2	2.011	0.1673	4.995	16.48	34.69	59.6	91.01	129.3	174.2	283.5	420.3
$C_2=B_2^2A$	0.0344	0.00286	0.0856	0.282	0.594	1.02	1.538	2.22	2.985	4.86	7.20
C_2-D	0.0344	-0.0596	-0.1644	-0.2805	-0.406	-0.542	-0.692	-0.842	-1.015	-1.39	-1.80
e^{C_1-D}	1	1	1	1	1	1	1	1	1	1	1
e^{C_2-D}	$\frac{0.9662}{0.9662}$	$\frac{0.8893}{0.9421}$	$\frac{0.827}{0.8482}$	$\frac{0.7766}{0.7554}$	$\frac{0.738}{0.6665}$	$\frac{0.7076}{0.5815}$	$\frac{0.6907}{0.5006}$	$\frac{0.6783}{0.4308}$	$\frac{0.6771}{0.3624}$	$\frac{0.6839}{0.2491}$	$\frac{0.7408}{0.1653}$
$B_1\sqrt{A}$	0.1853	0.425	0.664	0.903	1.14	1.38	1.62	1.86	2.095	2.58	3.05
$B_2\sqrt{A}$	0.1853	-0.0535	-0.292	-0.531	-0.770	-1.01	-1.25	-1.488	-1.728	-2.205	-2.68
N_1	0.2067	0.4522	0.6523	0.7984	0.8931	0.949	0.978	0.9915	0.997	1	1
$1-N_1$	0.7933	0.5478	0.3477	0.2016	0.1069	0.051	0.022	0.0085	0.003	0	0
N_2	0.2067	-0.0603	-0.320	-0.547	-0.724	-0.847	-0.923	-0.965	-0.985	-0.998	-1
$1-N_2$	0.7933	1.0603	1.320	1.547	1.724	1.847	1.923	1.965	1.985	1.998	2
$R=e^{C_1-D}(1-N_1)$...	0.82	0.616	0.420	0.260	0.145	0.072	0.032	0.125	0.0044	0	0
$S=e^{C_2-D}(1-N_2)$...	0.82	1.000	1.119	1.168	1.150	1.073	0.953	0.847	0.72	0.494	0.326
$R+S$	1.64	1.616	1.539	1.428	1.295	1.145	0.985	0.8595	0.7244	0.494	0.326
$\frac{\theta}{T} = \frac{1}{8\sqrt{Ax}}(R+S)$.	0.785	0.773	0.736	0.683	0.62	0.547	0.471	0.41	0.348	0.236	0.156

Let

$$N_1 = \frac{2}{\sqrt{\pi}} \int_0^{B_1\sqrt{A}} e^{-z_1^2} dz_1 \quad \text{and} \quad N_2 = \frac{2}{\sqrt{\pi}} \int_0^{B_2\sqrt{A}} e^{-z_2^2} dz_2.$$

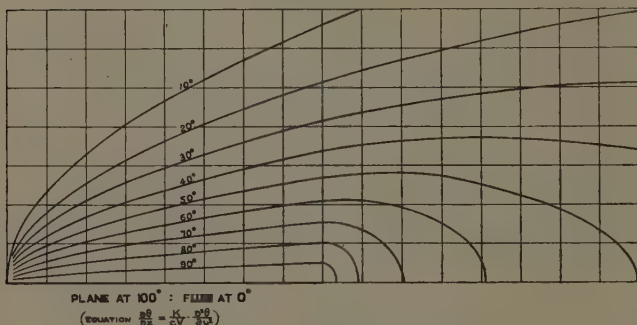
Then

$$\theta = \frac{1}{8\sqrt{Ax}} [e^{C_1-D}(1-N_1) + e^{C_2-D}(1-N_2)]. \quad (\text{vii.})$$

Values of N for given values of $B\sqrt{A}$ are obtained from the tables of de Morgan or Burgess.

In the present case a is found to be 0.0485 and b to be 0.0015, when T is 100° and the fluid is initially at 0° .

Fig. 3.



Now, choosing a fixed value of x , values of θ may be obtained at given values of y .

Table II. is a typical sheet of calculations for $x=4$, and the isotherms in the field near the plane and to the right of the plane are set forth in fig. 3.

A better solution, which does not involve the neglecting of $\frac{\partial^3 \theta}{\partial x^2}$, can be obtained by applying a method which

Dr. Thom of the University of Glasgow has used in solving aerodynamical problems*.

As bearing on the present problem it may be described thus:—

* Aero. Res. Comm., R. and M. 1194.

In the x, y field of temperature take a square ABCD of side $2n$ (fig. 4). Applying Taylor's Theorem,

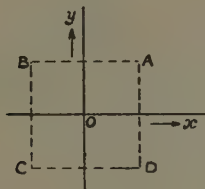
$$\theta_A = \theta_0 + n \frac{\partial \theta}{\partial x} + n \frac{\partial \theta}{\partial y} + \frac{1}{2} n^2 \left(\frac{\partial^2 \theta}{\partial x^2} + 2 \frac{\partial^2 \theta}{\partial x \cdot \partial y} + \frac{\partial^2 \theta}{\partial y^2} \right) + \dots$$

$$\theta_B = \theta_0 - n \frac{\partial \theta}{\partial x} + n \frac{\partial \theta}{\partial y} + \frac{1}{2} n^2 \left(\frac{\partial^2 \theta}{\partial x^2} - 2 \frac{\partial^2 \theta}{\partial x \cdot \partial y} + \frac{\partial^2 \theta}{\partial y^2} \right) + \dots$$

$$\theta_C = \theta_0 - n \frac{\partial \theta}{\partial x} - n \frac{\partial \theta}{\partial y} + \frac{1}{2} n^2 \left(\frac{\partial^2 \theta}{\partial x^2} + 2 \frac{\partial^2 \theta}{\partial x \cdot \partial y} + \frac{\partial^2 \theta}{\partial y^2} \right) + \dots$$

$$\theta_D = \theta_0 + n \frac{\partial \theta}{\partial x} - n \frac{\partial \theta}{\partial y} + \frac{1}{2} n^2 \left(\frac{\partial^2 \theta}{\partial x^2} - 2 \frac{\partial^2 \theta}{\partial x \cdot \partial y} + \frac{\partial^2 \theta}{\partial y^2} \right) + \dots$$

Fig. 4.



therefore

$$\Sigma \theta_A = 4\theta_0 + 2n^2 \left(\frac{\partial^2 \theta}{\partial y^2} + \frac{\partial^2 \theta}{\partial x^2} \right) \text{ approximately,}$$

for the third order terms completely disappear.

Therefore

$$\theta_0 = \frac{\Sigma \theta_A}{4} - \frac{1}{2} n^2 \cdot \nabla_{xy}^2 \theta.$$

But

$$\nabla_{xy}^2 \theta = \frac{cV}{K} \cdot \frac{\partial \theta}{\partial x} \quad \text{and} \quad \frac{cV}{K} = \frac{1}{4};$$

therefore

$$\theta_0 = \frac{\Sigma \theta_A}{4} - \frac{1}{8} n^2 \cdot \frac{\partial \theta}{\partial x}.$$

If values of θ are allotted in the first place by guesswork to the points A, B, C and D, then, provided the magnitude of n is suitable, the value obtained for θ_0 by applying the formula is in general a better approximation to the

true temperature at 0 than θ_A , θ_B , θ_C , and θ_D are to the true temperatures at A, B, C, and D. Starting with a network of values such as θ_A , the secondary network of values such as θ_0 yields a new set of values at A, B, C, D, etc. Thus, working to known boundary conditions, the values converge to those of the true field.

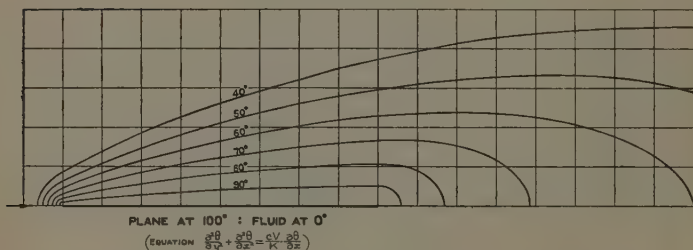
The process is laborious, particularly so in this case, in which convergence is very slow.

The result given in fig. 5 is carried to a fair degree of approximation.

For a hot body in a perfect fluid in cross-flow in which the stream-lines and equipotential lines are those of constant α and constant β and the temperature is θ ,

$$\nabla_{\alpha\beta}^2 \theta = \frac{cV}{K} \cdot \frac{\partial \theta}{\partial \beta}.$$

Fig. 5.



Since this is exactly the form of the equation in x and y for fluid passing a hot plane surface, if the system of α and β lines is available, the solution of fig. 5 can be simply transferred to the α , β field. The α , β system for fluid flowing past a cylinder has already been obtained by Dr. Thom by an application of his method. The values of θ obtained by a further application of the same method in the x , y field round a plane, as in fig. 5, are transferred to the α , β system in fig. 6.

The result would tend to show a minimum value of the temperature gradient along the normal to the surface at the upstream generator of the cylinder, implying a minimum rate of heat transfer from the surface at that point; but further refinement of the θ values by applying

* *Vide* Russell, Phil. Mag. xx. p. 591 (1910).

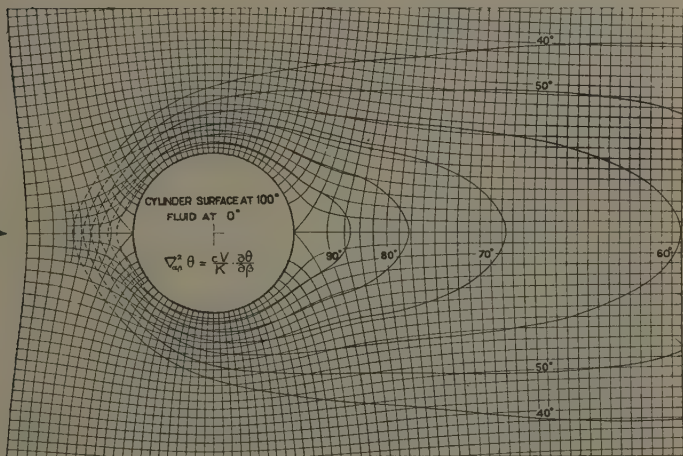
the above method many times over (a task demanding much time), is required to prove this point.

The temperature distribution of fig. 6 resembles the measured distribution round a horizontal cylinder under conditions of natural convection*.

*The Measurement of Temperatures in an Air Current
Flowing across a Hot Cylinder.*
(Forced Convection.)

The cylinder was of brass, $4\frac{1}{2}$ inches diameter, and was placed vertically across an air channel of approximately

Fig. 6.



2 ft. square section as shown in fig. 7. It was heated internally by steam at atmosphere pressure, and so mounted as to be capable of turning about its axis. The temperatures of the air in the vicinity of its surface were measured by means of a platinum wire of 0.003 in. diameter, stretched between two thin sheet brass arms and lying parallel to the axis of the cylinder. A similar short element of wire was introduced with the compensating leads. The arms were insulated from the

* *Vide* Ray. Proc. Indian Soc. Cultivation Sci. vi. p. 95 (1920); or McAdam's 'Heat Transformation,' p. 211 *et seq.* (1933).

Fig. 7.

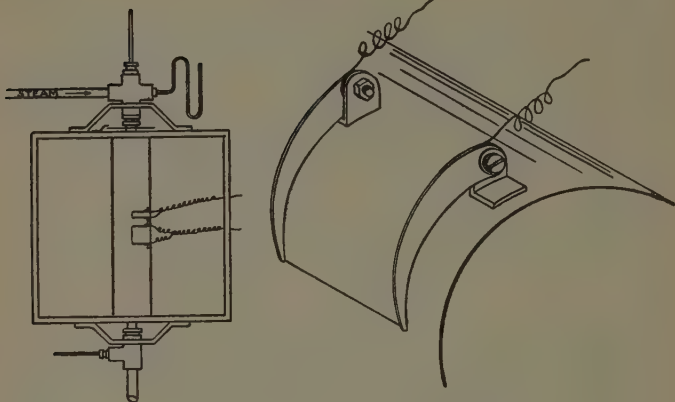
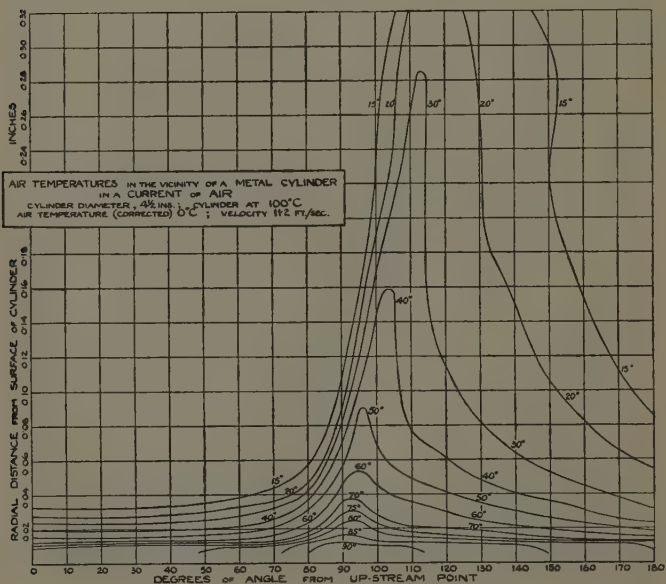


Fig. 8.



cylinder by fibre bushes and washers. They were adjustable so that the distance of the wires from the surface could be regulated. Numerous readings were made, and the results obtained are given in fig. 8.

There is a characteristic thickening of the hot boundary layer of air towards the sides of the stream. Since

$-\left(\frac{\partial\theta}{\partial n}\right)_{n=0}$ is a measure of the rate of heat flow at the

surface (n being the distance measured along the normal), these isotherms confirm observations obtained elsewhere of the low rate of heat flow from the flanks of the cylinder.

III. *Nuclear Synthesis and Isotopic Constitution.* By HAROLD J. WALKE, *M.Sc., A.Inst.P., Demonstrator in Physics, Washington Singer Laboratories, University College, Exeter* †.

I. *Introduction.*

IN a recent paper ‡, from considerations of nuclear disintegrations, an explanation has been put forward of the formation of the elements in nebular or stellar bodies. It was shown that, in the main, the elements were evolved as the result of a continuous synthesis due to the β -radioactivity of missing isotopes, supposed unstable. Progressive synthesis among the light elements was also shown to result from the absorption of protons, dipions, or α -particles into nuclei, but certain cases, notably the direct synthesis from lithium to beryllium and boron to carbon, were only explicable by assuming that the unknown isotopes Li_3^8 and B_5^{12} were radioactive and produced Be_4^8 and C_6^{12} , emitting β -rays. It was further shown that, in general, progressive synthesis, especially among the heavier elements, was only explicable by the β -ray activity of missing isotopes, unless excessively high stellar temperatures were assumed, since experimental evidence indicates that the highest energy protons and α -particles have not yet been observed

† Communicated by Professor F. H. Newman, D.Sc.

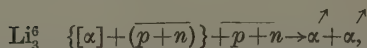
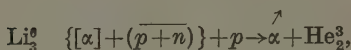
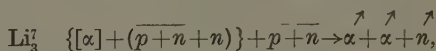
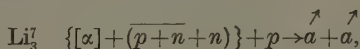
‡ Walke, *Phil. Mag.* xviii. p 795 (1934).

to disintegrate elements of atomic number greater than that of potassium. Proof of the general correctness of this process is afforded from the recent experimental work of Fermi on induced β -ray activity, produced by bombarding elements with neutrons, missing isotopes being formed under this bombardment.

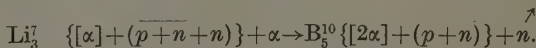
Formerly it was supposed† that stellar synthesis occurred by the absorption of protons and electrons by nuclei, the new nuclei formed when a proton is captured being stable. The induced radioactivity with positron emission of radionitrogen, formed by bombarding C_6^{12} with protons, suggests that this is not so, and it has been shown‡ that nuclei containing a free proton are radioactive. Recent experimental evidence, therefore, suggests that nuclear synthesis in stars results from actions involving protons, neutrons, dipions, and α -particles, rather than protons and electrons.

Direct synthesis of beryllium from lithium, as indicated below, can only occur by neutron absorption.

It has been demonstrated by several investigators that under proton and dipion bombardment the lithium isotopes disintegrate as below :—



and that under bombardment by high energy α -particles neutrons are emitted as follows :—



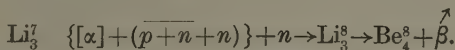
Hence progressive synthesis of the elements above lithium could not occur in stars, except at excessively high temperatures corresponding to the formation of B_5^{10} by neutron emission. It is therefore evident, especially in view of the recently reported experiments of Fermi §,

† d'E. Atkinson, *Astrophys. Journal*, lxxiii. p. 275 (1931).

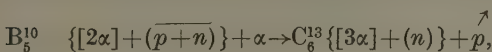
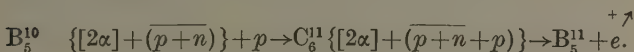
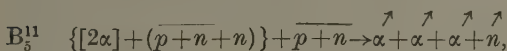
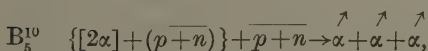
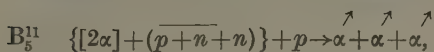
‡ Walke, *Phil. Mag.* xviii. p. 154 (1934).

§ Fermi, 'Nature,' cxxxiii. p. 1 (1934).

that the synthesis of beryllium occurs as a result of the β -ray radioactivity of Li_3^8 , formed when Li_3^7 absorbs a neutron, the action being



Similarly, as a result of the reactions



it was concluded that in stellar synthesis C_6^{12} was produced as a result of the β -radioactivity of B_5^{12} , formed when B_5^{11} captured a neutron.

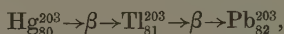
In applying the principle suggested by these reactions (which are essential to explain the direct synthesis of the elements in question), namely, that missing isotopes are short-lived β -radioactive links in a cosmic evolutionary process, it was found necessary to suggest that other stable isotopes existed which have not yet been detected. It is then possible to consider the synthesis of the isotopes by a single process, and it appears certain that the primary components of the nucleus are neutrons, diplons and α -particles being in many cases produced within the nucleus by the radioactivity of missing isotopes.

II. Spontaneous β -radioactive Isotopes.

To explain the synthesis of arsenic from germanium and selenium from arsenic, it was assumed that arsenic possessed a lighter isotope of mass 73, as well as the observed isotope As_{33}^{75} produced by the β -radioactivity of the missing Ge_{32}^{75} . Se_{34}^{74} would then result from the β -ray emission of the missing As_{33}^{74} . Recently it has been reported that the International Committee on Chemical Atomic Weights has adopted a new and lighter value

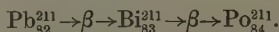
for the atomic weight of arsenic in lieu of the former value 74.93. This indicates that As_{33}^{73} may exist in small abundance, though on the present theory this would require the spontaneous β -radioactivity of Ge_{32}^{73} . However, while this action is possible, it will be shown later that Se_{34}^{74} may be produced otherwise. Other apparently definite cases of spontaneous β -radioactivity were indicated as follows.

The tin isotopes, which would be necessary to indicate the β -ray synthesis of antimony, are Sn_{50}^{121} and Sn_{50}^{123} . These isotopes would according to the theory be missing, but it is found that Sn_{50}^{121} exists in small abundance, though Sn_{50}^{123} is absent from the mass spectrum. It is therefore expected that weak β -ray activity of tin due to Sn_{50}^{121} will be detected. In addition, synthesis from mercury to thallium would be due to the β -radioactivity of Hg_{80}^{203} and Hg_{80}^{205} . Only the latter is missing, though the lighter isotope is present in only very slight abundance. It is therefore suggested that Hg_{80}^{203} spontaneously emits β -radiation. On this hypothesis Pb_{82}^{204} would be the lightest lead isotope corresponding to the β -radioactivity of the missing thallium isotope Tl_{81}^{204} . As, however, Pb_{82}^{203} exists in small abundance, Tl_{81}^{203} may also emit β -rays, and the following reactions are possible,

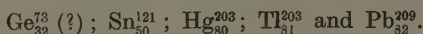


the new α -particle formed as a result of the double- β -ray synthesis completing the stable shell of 41α particles of the lead nucleus †.

The synthesis of bismuth on this scheme involves the β -radioactivity of Pb_{82}^{209} and Pb_{82}^{211} , the former producing Bi_{83}^{209} and the latter, since Bi_{83}^{211} is missing, Po_{84}^{211} as a result of the action

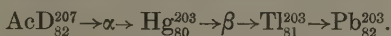


According to the scheme adopted, therefore, the isotopes discovered by Aston suggest that the following isotopes are spontaneously β -radioactive,



† Walke, Phil. Mag. xvii. p. 1176 (1934).

The supposed end product of the actinium series Pb_{82}^{207} may also be radioactive, the following actions occurring :—



The nucleus formed by the 0.03 per cent. of the atoms, following the $\text{AcC} \rightarrow \text{C}' \rightarrow \text{D}$ branch being excited by the emission of the swift α -particle from AcC' , the AcD so formed differs from Pb_{82}^{207} in being in a state of excess energy and thus emits another α -particle to produce Hg_{80}^{203} and finally Pb_{82}^{203} , the vacant place in the complete α -particle shell due to the initial α -ray emission of AcD being filled in by the new α -particle formed by the two succeeding β -ray transformations.

III. *Short-lived Radioactive Series among the Light Elements.*

Some difficulty was experienced in considering the isotopic constitution of krypton, zirconium, molybdenum, ruthenium, tin, xenon, and mercury, as all these elements possess lighter isotopes than would be expected by synthesis due entirely to the radioactivity of the missing isotopes of the preceding elements in the periodic table.

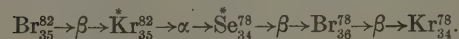
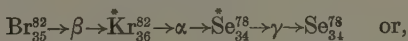
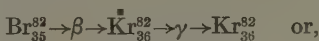
For example, in the case of krypton synthesis proceeds as a result of the β -ray emission of the missing bromine isotopes Br_{35}^{80} and Br_{35}^{82} , formed when the stable isotopes capture neutrons, and we should therefore expect Kr_{36}^{80} to be the lightest krypton isotope. But there is evidence that Kr_{36}^{78} exists as a stable isotope.

In order to explain this result it must be remembered that the emission of β -rays from an element of odd atomic number results in the formation of a new α -particle in the nucleus †, and the mass defect energy released in such an action is very great. Among the normally radioactive atoms it has been shown ‡ that in all such reactions an excited nucleus is produced as a result of the excess energy released. The excited nucleus returns to the normal state by emitting γ -radiation or in some cases emits almost immediately the α -particle produced, as in the case of the short-lived C' bodies. In the case of the elements now being considered we therefore assume that the new nucleus formed by the initial

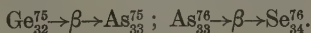
† Walke, *loc. cit.*

‡ Walke, *loc. cit.*

β -ray disintegration of the Br_{36}^{82} isotope is formed in a highly excited state Kr_{36}^{82*} , as a result of the production of the new α -particle, and that, in general, it emits its excess energy in returning to the stable nucleus Kr_{36}^{82} in the form of γ -radiation. It is suggested, however, that a small percentage of the excited nuclei emit the newly formed α -particle almost at once and produce, thereby, an excited nucleus Se_{34}^{78*} which differs from the normal Se_{34}^{78} produced when Se_{34}^{77} captures a neutron. This nucleus emits its excitation energy either in the form of γ -radiation or, if this is converted inside the nuclear potential field, to produce an electron pair[†], changes to Br_{35}^{78} by emitting an electron. This unstable bromine nucleus then produces Kr_{36}^{78} by a second β -ray transformation. Thus we have as it were a short-lived radioactive series:—



It is also possible that some of the newly formed Kr_{34}^{78} nuclei emit the α -particle formed by the double β -ray transformation to produce Se_{34}^{74} , which exists in small abundance. On this hypothesis, therefore, the suggested β -radioactivity of Ge_{32}^{73} and the existence of As_{33}^{73} (see section ii.) would not be necessary to explain the presence of Se_{34}^{74} (which isotope would not be expected from the direct synthesis process due to the β -ray activity of the known "missing" isotopes Ge_{32}^{75} and As_{33}^{76}) i. e.,



However, it is very doubtful whether krypton is sufficiently abundant to explain the complete synthesis of Se_{34}^{74} from Kr_{36}^{78} , and it would therefore appear that the synthesis of this isotope does proceed as suggested by the instability of As_{33}^{74} . We conclude, therefore, that the abundance of arsenic, selenium and krypton, and the presence of Se_{34}^{74} suggest that arsenic may possess

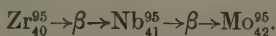
[†] Walke, *loc. cit.*

a less abundant isotope of mass 73 and that germanium may be feebly β -ray radioactive.

It is to be emphasized that the proposed action does not involve the spontaneous α -ray radioactivity of the stable isotopes Kr_{36}^{82} and Kr_{36}^{78} . It is merely suggested that, when formed initially, the nuclei are in a state of excitation as the result of the mass defect energy released by the formation of the new α -particle. In the majority of such transformations the α -particle is bound within the nucleus, the excess energy being emitted in the form of γ -radiation; in a certain number of such nuclei, however, the excess energy is emitted in the form of kinetic energy of the newly formed α -particle. This " α -radioactivity" is therefore, as it were, induced by the excitation energy and might be detected in transmutation experiments such as have been performed by Fermi. It does not involve the radioactivity of the stable isotopes Kr_{36}^{82} and Kr_{36}^{78} .

Considering the group of elements zirconium, niobium, masurium, and ruthenium, the isotopes found by means of the mass spectrograph suggest that these isotopes are related by a short-lived radioactive series arising in the initial synthesis of the elements in stars and perhaps reproducible if the parent nucleus is formed by neutron bombardment of certain stable isotopes.

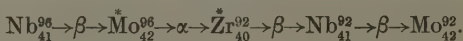
Among the zirconium isotopes Zr_{40}^{93} and Zr_{40}^{95} are missing, and these, according to the synthesis process, produce Nb_{41}^{93} and Nb_{41}^{95} . The latter has not been detected, but the chemical atomic weight of the element and the fact that Zr_{40}^{95} is missing suggest that this isotope is present in small abundance. Synthesis would then proceed by the β -ray radioactivity of Nb_{41}^{94} and Nb_{41}^{96} , the new isotopes being Mo_{42}^{94} and Mo_{42}^{96} . It is, of course, possible that Nb_{41}^{95} is itself a β -ray isotope of long life which produces Mo_{41}^{95} , so that Nb_{41}^{95} may not exist, the synthesis action being



The chemical atomic weight, however, indicates the presence of a heavier isotope, and the presence of this isotope would allow the synthesis of Mo_{42}^{92} , as will be indicated. However, the presence of Nb_{41}^{95} is not essential

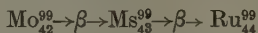
to the theory, as will be shown when considering ruthenium.

Thus if Nb_{41}^{95} is stable, or at least of sufficiently long life to allow the formation of the β -ray emitter Nb_{41}^{96} , then Mo_{42}^{92} can be synthesized as with krypton, for the isotope Mo_{42}^{96} produced by the radioactivity of Nb_{41}^{96} might occasionally emit the newly formed α -particle to produce the excited Zr_{40}^{92} . This nucleus then produces Mo_{42}^{92} as the result of β -ray disintegration, the action being

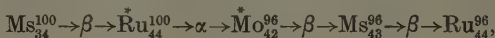


This reaction and explanation of the presence of Mo_{42}^{92} depends on the stability, or comparatively long life, of Nb_{41}^{95} allowing the formation of the unstable Nb_{41}^{96} by neutron capture. An alternative method of the formation of Mo_{42}^{92} is as follows.

In the molybdenum group of isotopes Mo_{42}^{99} is missing, and so is Mo_{42}^{101} . These two isotopes are therefore the β -ray radioactive links in the general synthesis process and produce the two possible masurium isotopes Ms_{43}^{99} and Ms_{43}^{101} . It is probable that both isotopes exist, though the comparatively high abundance of Ru_{44}^{99} may be evidence to show that the isotope Ms_{43}^{99} is missing, this nucleus being β -radioactive (though of comparatively long life), so that the action



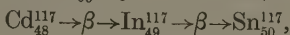
takes place. However, the presence of Ru_{44}^{96} and the abundance of Ru_{44}^{100} suggest that if Ms_{43}^{99} is unstable and does not exist, it was of sufficiently long life to allow the formation of the β -ray radioactive isotope Ms_{43}^{100} . The unstable isotope produces Ru_{44}^{100} , and as the reaction causes the formation of a new α -particle, we suggest that a few of the nuclei Ru_{44}^{100} formed with excess energy emit immediately the newly formed α -particle, the action being the same as that suggested to explain the presence of the lighter krypton and selenium isotopes. Thus we have



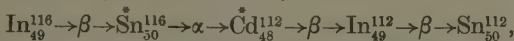
and if we suppose that similarly Ru_{44}^{96} when formed in the excited state occasionally emits the newly formed α -particle, then Mo_{42}^{92} can be so produced.

The isotopes of zirconium, molybdenum, and ruthenium would therefore suggest that both niobium and masurium consist of two isotopes, viz., Nb_{41}^{93} , Nb_{41}^{95} and Ms_{43}^{99} and Ms_{43}^{101} . However, as has been shown, the presence of Nb_{41}^{95} and Ms_{43}^{99} are not essential to the synthesis process, it merely being required that these isotopes, if missing, should have had sufficiently long life to allow the production of the unstable isotopes Nb_{41}^{96} and Ms_{43}^{100} . It may, however, be suggestive that Mo_{42}^{92} exists in comparative abundance. This would suggest that it is formed both from Mo_{42}^{96} and from Ru_{44}^{96} .

The cadmium isotope of mass number 115 is missing, and on the theory suggested is the synthesis link producing In_{49}^{115} by β -ray emission, the element indium being apparently single. Thus Cd_{48}^{117} , produced when Cd_{48}^{116} captures a neutron, produces Sn_{50}^{117} by the double β -ray synthesis,



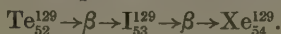
the missing isotope In_{49}^{117} being β -radioactive. The lightest isotope of tin by direct β -ray synthesis is Sn_{50}^{116} , formed by the disintegration of In_{49}^{116} , which results when In_{49}^{115} captures a neutron. However, Sn_{50}^{112} exists, so that we suggest it is formed by an action similar to those we have already discussed, viz.,



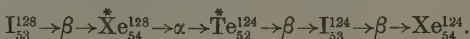
the nuclei Sn_{50}^{116} and Cd_{48}^{112} with excess energy disintegrating as shown. The unstable isotope In_{49}^{117} may be of sufficiently long life to allow the production of the β -ray isotope In_{49}^{118} , and this isotope may give rise to Sn_{50}^{114} by the action



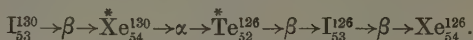
A further example of the process under discussion is given by xenon. Though both tellurium isotopes Te_{52}^{127} and Te_{52}^{129} are missing, iodine itself is only a single element of mass number 127. Thus I_{53}^{129} is itself a short-lived β -radioactive isotope and we have



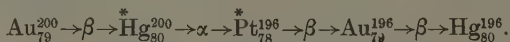
The missing iodine isotope I_{53}^{128} is β -radioactive and Xe_{54}^{128} is produced. However, occasionally the newly formed nucleus emits its excess energy as kinetic energy of the newly formed α -particle, so we have



Though I_{53}^{129} is missing as suggested, it is probable that this isotope has a sufficiently long life for it occasionally to capture a neutron to produce the very unstable nucleus I_{53}^{130} , which gives rise to Xe_{54}^{130} and also Xe_{54}^{126} according to the action



The final example of the process is the production of Hg_{80}^{196} . The probable gold isotopes are Au_{79}^{197} and Au_{79}^{199} , and the missing isotopes of mass number 198 and 200 are the synthesis links in the general evolutionary process resulting in the formation of Hg_{80}^{198} and Hg_{80}^{200} . The isotope of mass 200 when formed in its state of excess energy generally transforms to the stable state by emitting γ -radiation. In a small percentage of nuclei, however, the newly formed α -particle is emitted on formation, and the excited Pt_{78}^{196} nucleus so produced is transformed by a double β -ray change into Hg_{80}^{196} as follows :—



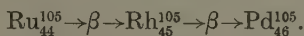
Thus we can account for the additional isotopes which would not be expected in a general β -ray synthesis of the elements, by a very probable process and without presupposing any additional stable isotopes in the whole range from hydrogen to the radioactive elements, with the possible exceptions of As_{33}^{73} and Nb_{41}^{95} , and admitting the probability that masurium consists of two isotopes of mass numbers 99 and 101. While, however, the chemical atomic weights favour the probable existence of these isotopes, the processes discussed indicate that they are not essential to the general synthesis theory developed. It is therefore apparent that As_{33}^{73} , Nb_{41}^{95} , Ms_{43}^{99} and Ms_{43}^{101} may exist, the first two if stable being present in small abundance. These isotopes, if missing, were comparatively long lived during the evolutionary

process, though they may have disappeared completely now. Evidence favours the idea that Kr_{36}^{78} , Mo_{42}^{92} , Ru_{44}^{96} , Sn_{50}^{112} , Sn_{50}^{114} , Xe_{54}^{124} , Xe_{54}^{126} , Hg_{80}^{196} , and probably Se_{34}^{74} were formed indirectly, rather than in the direct line of progressive synthesis.

IV. *Isotopes of Rhodium, Palladium, and Cadmium.*

The isotopes of palladium have not yet been determined by Aston with the mass spectrograph. In considering the general synthesis process we may, however, discuss the probable isotopes of this element, especially in view of the discussion given in the last section, as we can thereby consider lighter small abundance isotopes as we did with Sn_{50}^{112} .

The ruthenium isotope Ru_{44}^{103} is missing and the heaviest stable isotope of ruthenium has mass number 104. By the theory of progressive synthesis, Ru_{44}^{103} and Ru_{44}^{105} formed when the stable isotopes Ru_{44}^{102} and Ru_{44}^{104} capture neutrons, are β -radioactive and produce the rhodium isotopes Rh_{45}^{103} and Rh_{45}^{105} . The atomic weight of rhodium is, however, 102.9, so that, as would be expected, Aston † has recently shown that it is single of mass number 103 and Rh_{45}^{105} is itself probably β -radioactive, though this isotope may be of comparatively long life. Thus we have



By the direct synthesis from the missing rhodium isotope of mass 104 the lightest abundant palladium isotope is produced, viz., Pd_{46}^{104} . The processes discussed in the last section, however, suggest that occasionally Pd_{46}^{104} may emit the newly formed α -particle, so that the lightest palladium isotope may have mass number 100, though it would probably be in small abundance. In addition, though Rh_{45}^{105} is missing, it may have a sufficiently long life to produce the unstable Rh_{45}^{106} , which emits β -radiation and is transformed to Pd_{46}^{106} . As this isotope may also occasionally emit an α -particle, if produced as suggested, a light isotope of mass number 102 may exist. As the next element silver has two isotopes of mass 107 and 109 the theory suggests that isotopes of palladium of

† Aston, 'Nature,' cxxxiii. p. 684 (1934).

corresponding mass are missing. Hence we conclude that palladium consists of the following isotopes :—

100 (?), 102 (?), 104, 105, 106, 108 and perhaps 110, the order of decreasing abundance being 106, 105, 104, 108, 110 (?), 100 (?), and 102 (?).

Synthesis to cadmium results from the β -radioactivity of the missing isotopes Ag_{47}^{108} and Ag_{47}^{110} , produced when the stable isotopes capture neutrons. In consequence Cd_{48}^{108} and Cd_{48}^{110} are produced, though the former has not been detected. It is therefore apparent that either this isotope is stable, but has not yet been observed, or that it emits the newly formed α -particle resulting from the β -ray change producing Pd_{46}^{104} . Moreover, it is possible, if this isotope is stable, that Cd_{48}^{104} and Cd_{48}^{106} are also present in small abundance, these isotopes being formed as suggested in section III. Cadmium is difficult to deal with in the mass spectrograph, and its mass spectrum lies near the limit of resolution. In consequence Cd_{48}^{108} , which is probably stable, may have been missed. It is thus apparent that three additional cadmium isotopes may exist, namely, Cd_{48}^{108} , Cd_{48}^{106} , and Cd_{48}^{104} . If these isotopes are stable the last two will be present only in slight abundance, though it would be anticipated that Cd_{48}^{108} , if it exists, would be in sufficient abundance to be detectable†. However, as indicated, the absence of this isotope may be real, as it may at the moment of formation emit its α -particle to produce Pd_{64}^{104} .

V. *Synthesis of the Elements from Argon to Copper.*

Synthesis to argon results from the β -radioactivity of the missing chlorine isotopes Cl_{17}^{36} and Cl_{17}^{38} , the new nuclei being Ar_{18}^{36} and Ar_{18}^{38} . The latter isotope was recently observed by Zeeman. Ar_{18}^{39} , however, is the next β -radioactive link and produces K_{19}^{39} . Synthesis from potassium proceeds by the radioactivity of K_{19}^{40} and K_{19}^{42} , both isotopes being missing. In addition, since K_{19}^{41} may be β -radioactive we should expect the following isotopes of calcium of mass numbers 40, 41, 42, 43, and 44. Recently Aston‡ has redetermined

† Note added in proof.

‡ Aston, 'Nature,' cxxxiii. p. 869 (1934).

the mass spectrum of calcium and has definitely observed Ca_{20}^{42} and Ca_{20}^{43} , but concludes from the absence of Ca_{20}^{41} that K_{19}^{41} is not the β -radioactive potassium isotope. According to the hypothesis of progressive synthesis K_{19}^{40} and K_{19}^{42} are both β -radioactive and either of these isotopes may be present in small abundance and cause the β -ray emission of this element.

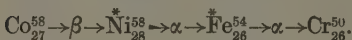
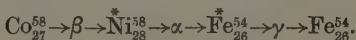
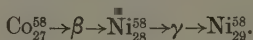
From calcium the radioactivity of Ca_{20}^{45} results in the formation of scandium Sc_{21}^{45} , which element has been shown to be single. The missing isotope Sc_{21}^{46} therefore emits β -radiation and Ti_{22}^{46} is produced. In the first discussion of the synthesis process† the single titanium isotope Ti_{22}^{48} introduced difficulties, but the newly detected isotopes of mass number 46, 47, 49, and 50 remove the difficulties and allow the direct synthesis as follows. The missing Ti_{22}^{51} formed when Ti_{22}^{50} captures a neutron, emits β -rays to produce the single element V_{23}^{51} and the next synthesis to chromium results from the β -ray emission of V_{23}^{52} . We should thus expect Cr_{24}^{52} to be the lightest chromium isotope. However, as Cr_{24}^{50} exists we anticipate that it was formed by a secondary process, as will be indicated later in this section.

The heaviest stable chromium isotope Cr_{24}^{54} when it captures a neutron produces the missing and β -radioactive isotope Cr_{24}^{55} , which spontaneously transforms to Mn_{25}^{55} . Synthesis to iron results from the β -ray activity of Mn_{25}^{56} , which produces Fe_{26}^{56} . There is, however, a lighter isotope of mass number 54; it is probable, as will be shown later, that this isotope is formed by the same secondary process which results in Cr_{24}^{50} .

The next iron isotope is Fe_{26}^{57} , and this is apparently missing. Cobalt, however, consists of only one isotope of mass number 59. If it possesses the lighter isotope Co_{27}^{57} in small abundance we can overcome the difficulty of Cr_{24}^{50} and Fe_{26}^{54} by applying the principles already suggested in section III. Thus if Co_{27}^{57} exists as a stable isotope, Fe_{26}^{57} will be missing (though Fe_{26}^{58} will probably exist in small abundance), and so will Fe_{26}^{59} be missing. The next synthesis will result from the β -radioactivity

† Walke, *loc. cit.*

of Co_{27}^{58} and Co_{27}^{60} , and as a result Ni_{28}^{58} and Ni_{28}^{60} are produced, the action in each case producing a new nuclear α -particle as shown below. If Ni_{28}^{58} is formed in a state of excess energy, as a result of the mass defect energy released, it is possible that some of the excited nuclei emit the excess energy in the form of kinetic energy of the newly formed α -particle, the majority of the nuclei, however, returning to the stable state Ni_{28}^{58} , by emitting high energy γ -radiation. Thus Fe_{26}^{54} would be formed, and as a result of the emission of the α -particle, this nucleus is produced in an excited state and may, in consequence, emit in some cases another α -particle to produce Cr_{24}^{50} . Thus we have, as it were, the possibility of a short radioactive series, the stable nuclei Ni_{28}^{58} , Fe_{26}^{54} , and Cr_{24}^{50} being produced as a result of the mass defect energy released in the initial β -ray transformation, viz.,



Hence if cobalt has a lighter isotope of mass 57 we can understand why Fe_{26}^{57} is missing and how the isotopes Ni_{28}^{58} , Fe_{26}^{54} , and Cr_{24}^{50} are formed.

Once more it is emphasized that the α -particle emission does not require that Ni_{28}^{58} and Fe_{26}^{54} should be spontaneously radioactive. The α -particle is emitted from some of the newly formed nuclei because of the excess energy released in the production of the new α -particle by the initial β -ray change.

The next element, copper, has two isotopes Cu_{29}^{63} and Cu_{29}^{65} and the corresponding nickel isotopes should be missing. Aston, however, has only observed Ni_{28}^{58} and Ni_{28}^{60} . It is significant that nickel is difficult to deal with in the mass spectrograph, so that it is possible that heavier isotopes exist. It would appear that Ni_{28}^{61} and Ni_{28}^{62} , and probably Ni_{28}^{64} , are stable and may be detected in the mass spectrum †.

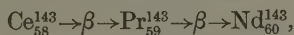
† Note added in proof.

Thus the latest work on mass spectra confirms the general β -radioactive synthesis considered, and though there is still the difficulty discussed with cobalt, it is apparent that new nickel, cobalt, and iron isotopes will probably be found.

VI. *Synthesis of the Rare Earths.*

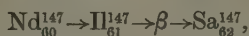
Aston's recent work on the isotopic constitution of the rare earth group of elements also confirms the synthesis process and shows in detail the progressive evolution of these elements by the β -radioactivity of missing isotopes as below.

In the barium group there are no isotopes missing from mass number 135 to 138. Synthesis to lanthanum is by the β -radioactivity of Ba_{56}^{139} . Lanthanum is very probably a single element of mass number 139, as would be indicated by its chemical atomic weight 138.90. By neutron absorption La_{57}^{140} is produced, this isotope being radioactive to form Ce_{58}^{140} . Cerium gives only two isotopes in its mass spectrum of mass numbers 140 and 142, synthesis to praseodymium resulting from the missing isotope Ce_{58}^{141} . Pr_{59}^{141} is the only praseodymium isotope, so that Ce_{58}^{143} , resulting from the nucleus Ce_{58}^{142} when a neutron is captured, gives rise to neodymium as a result of the double β -ray change,



so that we should expect a neodymium isotope of mass 143.

The missing isotope Pr_{59}^{142} is the next β -radioactive link, so that the lightest neodymium isotope would be Nd_{60}^{142} . Aston † has reported the following isotopes 142, 143, 144, 145 and 146, so that the missing 147 is probably the next isotope which is radioactive to produce the missing element of atomic number 61, viz., illinium. It is significant that samarium has an isotope of this mass number (which would not be expected if II_{61}^{147} were stable), so that illinium may be spontaneously β -radioactive. It may thus be the source of the recently reported ‡ β -ray. activity of neodymium. Thus we have



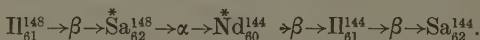
† Aston, 'Nature,' cxxxiii. p. 684 (1934).

‡ Libby, Phys. Rev. xlv. p. 845 (1934).

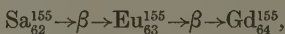
the β -ray change from illinium to samarium being one of long life. Thus the β -ray activity of neodymium may be due to illinium impurity.

It is interesting to notice that samarium spontaneously emits α -particles. It is possible that the action is related to the supposed β -ray activity of illinium, as by this form of activity Sa_{62}^{147} is formed in a state of excess energy as a new α -particle is produced in the nucleus. The spontaneous emission of α -particles from samarium may thus be due to the isotope Sa_{62}^{147} formed from illinium Il_{61}^{147} present as impurity, the resulting nucleus being Nd_{60}^{143} .

Synthesis of samarium would, however, result from the radioactivity of the missing Il_{61}^{148} , the new isotope being Sa_{62}^{148} , and this would be the lightest isotope in a direct synthesis process. In view of the presence of 147 it thus appears highly probable that Il_{61}^{147} is spontaneously radioactive. In addition, as Aston† has more recently reported the presence of 144 in small abundance, this isotope probably arises as suggested in section III, the newly formed Sa_{62}^{148} when formed in a state of excess energy emitting an α -particle according to the action,



The mass range covered by the samarium isotopes is thus 144 and 147–150, and 152 and 154, with 151 and 153 missing. These isotopes are β -radioactive on the theory under discussion, and produce the europium isotopes Eu_{63}^{151} and Eu_{63}^{153} . Samarium 155 on this hypothesis would give rise to the double β -ray change,

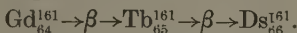


while the missing isotopes Eu_{63}^{152} and Eu_{63}^{154} would, by β -ray synthesis, produce the gadolinium isotopes of corresponding mass number. Aston has observed such isotopes of gadolinium, but thinks they may be due to samarium impurity. According to the synthesis process suggested, however, these isotopes are possible.

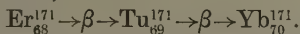
Gadolinium has mass numbers 152 and 154 to 160 with 159 missing. This isotope and Gd_{64}^{161} would be the

† Aston, 'Nature,' cxxxiii. p. 684 (1934).

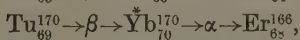
β -radioactive links to produce corresponding isotopes of terbium. Aston has, however, only observed Tb_{65}^{159} , so that it appears probable that Gd_{64}^{161} gives rise to the double β -ray change,



We should thus expect the lightest dysprosium isotope to have mass number 160 corresponding to the missing terbium isotope of the same mass. Aston† has not detected this isotope, but it probably exists as a stable nucleus. The mass range of this element then extends from 160 to 164. Ds_{66}^{165} is missing and is the β -radioactive link producing holmium 165. This element is single, and the unstable isotope Ho_{67}^{166} produced when Ho_{67}^{165} captures a neutron emits β -radiation, and is transformed to Er_{68}^{166} . This element consists of four isotopes with mass numbers 169 and 171 missing. These should produce Tu_{69}^{169} and Tu_{69}^{171} , but the latter is missing. It, too, is probably β -radioactive, so that the double β -ray change occurs,

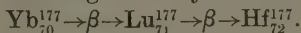


The missing Tu_{69}^{170} is on the theory β -radioactive and should produce the lightest ytterbium isotope of mass 170. This isotope has not yet been detected. It is possible, of course, that the following actions occur, so that the isotopes Ds_{66}^{160} and Yb_{70}^{170} may not be stable, thus



the newly formed α -particle being emitted from the nucleus with excess energy due to the mass defect energy released in the formation of the α -particle. Otherwise we should expect Ds_{66}^{160} and Yb_{70}^{170} to be observed as stable isotopes present in small abundance.

The missing ytterbium isotopes of mass number 175 and 177 are β -radioactive, according to the theory, producing Lu_{71}^{175} and Lu_{71}^{177} . This isotope of mass number 177 is also missing, so that again we have a double β -ray transformation resulting in the synthesis of Hf_{72}^{177} thus,



† Aston, *loc. cit.*

Lucetium being a single element of mass number 175, the missing isotope Lu_{71}^{176} formed when the stable isotope captures a neutron, emits β -radiation and produces Hf_{72}^{176} . As would be expected this element has isotopes of mass numbers 176, 177, 178, 179, and 180, the missing isotope Hf_{72}^{181} being the β -radioactive link producing tantalum Ta_{73}^{181} . This isotope on capturing a neutron produces Ta_{73}^{182} , which emits β -radiation and is transformed to tungsten W_{74}^{182} .

It can thus be seen that the rare earth group of elements illustrates very well the suggested synthesis process whereby the elements were evolved primarily by neutron capture and β -radioactivity. The progressive synthesis is very definitely shown in this group, as there is, corresponding to each element of odd atomic number, a missing isotope of even atomic number and, except for the cases discussed, there are corresponding links between the odd numbered elements and the next element of even atomic number.

VII. *Isotopes of the Elements Osmium, Iridium, and Gold.*

Aston has recently determined the isotopes of osmium by means of the second mass spectrograph. Its heaviest isotope, as indicated in the mass spectrum, had a mass 192 with 191 and 193 missing. The atomic weight of osmium, calculated by means of the mass spectrum, is 190.31, a value which is considerably less than its chemical value 190.8, which suggests either that the chemical value is wrong or that a heavier isotope Os_{76}^{194} exists. As the weak isotopes Os_{76}^{186} and Os_{76}^{187} were observed, it appears likely that Os_{76}^{192} is the heaviest stable isotope of osmium and that therefore iridium consists of two isotopes, Ir_{77}^{191} and Ir_{77}^{193} . The chemical atomic weight indicates that iridium consists of the isotopes Ir_{77}^{193} and Ir_{77}^{195} in small abundance. From the mass spectrum of osmium it appears that the chemical value of the atomic weight of iridium is also in error, this element consisting of the isotopes Ir_{77}^{191} (in small abundance) and Ir_{77}^{193} . It is, of course, possible that Aston has not observed Os_{76}^{191} , and that iridium consists of a single isotope of mass 193. At the present stage,

however, it appears that iridium has two isotopes of mass number 191 and 193.

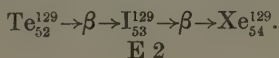
Synthesis of platinum then results from the β -radioactivity of the missing iridium isotopes 192 and 194, so that we should expect platinum to possess isotopes of mass numbers 192, 193 (?), 194, 195, 196, and 198, with the doubtful possibility of small abundance isotopes of mass number 188 and 190, produced by the secondary process indicated in section III. The order of decreasing abundance of these nuclei is probably 196, 195, 194, 198, 192, 193 (?), 190 (?), 188 (?). The missing isotopes in this mass range Pt_{78}^{197} and Pt_{78}^{199} are the β -radioactive isotopes, which produce the gold isotopes of mass 197 and 199. Synthesis to mercury then proceeds as a result of the β -ray activity of Au_{79}^{198} and Au_{79}^{200} .

We thus conclude that osmium either has isotopes of mass 191 and 194, in which case the chemically determined values of the atomic weight of osmium and iridium are probably correct, or that the isotope of mass 191 is missing, as found by Aston, in which case the chemically determined values are too high. If the iridium isotopes have these mass numbers, platinum has a stable isotope of mass 192. If 193 is the lighter or the only iridium isotope, the main platinum range will start at mass number 194. The evidence so far obtained indicates that the iridium and platinum isotopes are as suggested above, and indicates that the chemically determined atomic weights are too high.

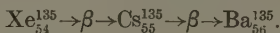
VIII. *Isotopes of Iodine and Cæsium and the Synthesis of the Radioactive Elements.*

The synthesis and isotopes of iodine and cæsium are interesting in connexion with the missing elements 85 and 87, and the synthesis of the radioactive elements as will be indicated.

Both the tellurium isotopes Te_{52}^{127} and Te_{52}^{129} are missing, indicating, according to the theory adopted, that these isotopes are β -radioactive and produce I_{53}^{127} and I_{53}^{129} . Aston has shown, however, that I_{33}^{129} is missing, iodine being a single element of mass 127, and in addition Xe_{54}^{129} is the most abundant isotope of xenon, so that we assume the synthesis process



Similarly the missing xenon isotopes are Xe_{54}^{133} and Xe_{54}^{135} , and these are the β -radioactive links which produce the caesium isotopes Cs_{55}^{133} and Cs_{55}^{135} . But, as with iodine, caesium is only a single element of mass number 133, so that we conclude that the heavier isotope Cs_{55}^{135} is itself β -radioactive to produce Ba_{56}^{135} by the action



This is to be expected when we consider the other alkali metals, for potassium and rubidium are both β -radioactive, the spontaneous activity being due to the heavier isotopes. Thus, as the heavier caesium isotope is missing, it is apparent that it, too, was β -radioactive, but of shorter life than the corresponding potassium and rubidium isotopes and has consequently disappeared.

We should thus expect eka-caesium to be a single element as its heavier isotope would be short lived and, correspondingly, we should expect eka-iodine to be single.

It is interesting to notice that on this hypothesis Cs_{55}^{134} would be β -radioactive to produce Ba_{56}^{134} . Aston has determined the isotopic constitution of barium and states that the lightest isotope has a mass number 135. The value of the atomic weight calculated from his data is greater than the chemically accepted value, so that it is possible that the lighter isotope exists in small abundance. On the other hand, it is possible that Ba_{56}^{134} emits the newly formed α -particle produced by the β -ray change, so that this isotope may not be detected. The isotope resulting from the action would be Xe_{54}^{130} , but this exists in such small relative abundance that it would appear probable that Ba_{56}^{134} does exist, but has not been detected.

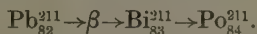
The radioactive elements on account of their instability present a problem to which attention must be paid in developing any theory of nuclear synthesis. As α -ray emission has only been definitely established for samarium and platinum among the stable elements, it seems definite that α -ray radioactivity is not a common property of the elements as the β -ray synthesis we have discussed, for which there is definite experimental evidence. The α -ray emission of these elements has been explained † by assuming a definite shell structure for the α -particles

† Walke, Phil. Mag. xvii. p. 1176 (1934).

in nuclei which are of greater atomic number than tin, and it has also been shown that the α -radioactivity of the elements of atomic number greater than 82 can be accounted for, at least qualitatively, by the addition of α -particles to the stable shell system which becomes complete for those isotopes in whose nuclei there are 41 α -particles. In order to account for the synthesis of the radio-elements, therefore, we need only apply the rules evident from the discussion already given, and which have received application in the isotopic configurations of the rare earth group of elements.

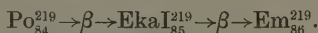
As the radio-active elements possess all the properties of the normal chemical elements, but differ from them in being unstable, we should expect those with even atomic numbers to consist of groups of isotopes, whereas those with odd atomic number should consist of one or at most two isotopes. With these facts in mind, and knowing that the atomic weights of thorium and uranium are 232.12 and 238.14 respectively, we can consider the synthesis of elements of atomic number 82-92 as follows (we neglect in this discussion the possible disintegration of the unstable isotopes produced, and consider the elements as if they were stable).

Omitting unstable isotopes of atomic number 81, which are produced by the disintegration of heavier isotopes of elements of higher atomic number, synthesis from lead to bismuth is due to the β -radioactivity of Pb_{82}^{209} and Pb_{82}^{211} , which should accordingly be missing. The former exists in small abundance, so that we anticipate that normal lead will be found to emit weak β -rays. In addition, as Bi_{83}^{211} is also missing from mass spectra, this isotope must also be β -radioactive, so that the double β -ray synthesis change occurs

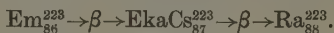


The lightest polonium isotope, however, is produced by the β -radioactivity of the missing Bi_{83}^{210} . We should thus expect the isotopes of this element to possess mass numbers 210, 211, 212, 213, 214, 215, 216, and 218, with 217 and 219 missing. Assuming as we are in this discussion that these nuclei are stable, synthesis to the next element, eka-iodine, is by the β -radioactivity of Po_{84}^{217} and of Po_{84}^{219} . By analogy with iodine we expect

the heavier isotope EkaI_{85}^{219} to be β -radioactive, so that the element would consist of a single isotope of mass 217, the double β -ray transformation of Po_{84}^{219} producing Em_{86}^{219} as follows :—

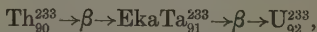


The lightest isotope of Emanation would be produced by the radioactivity of the missing EkaI_{85}^{218} , so that the isotopic constitution of this element of atomic number 86 is probably 218, 219, 220, and 222, the missing isotopes producing the isotopes of eka-cæsium by emitting β -radiation. As, however, the cæsium isotope of mass 135 is missing, we should expect, by analogy, that EkaCs_{87}^{223} is also β -radioactive, the double β -ray synthesis being



Thus eka-cæsium should be single consisting of the isotope of mass number 221 †.

The lightest radium isotope would be produced by the β -radioactivity of the missing EkaCs_{87}^{220} , so that the radium isotopes would have mass numbers 220, 221, 222, 223, 224, 226, and 228, with 225 and 227 the missing isotopes necessary for progressive synthesis to the next element actinium. The isotopes of this element of atomic number 89 would therefore have mass numbers 225 and 227. Synthesis to thorium would result from the β -radioactivity of the missing Ac_{89}^{226} and Ac_{89}^{228} . Thus thorium would consist of isotopes with mass numbers 226, 227, 228, 229, 230, 231, 232, 234, and 236 (?) if it were a stable element, the missing isotopes of mass 233 and 235 causing the evolution of the element of atomic number 91 by β -ray emission. The isotopes of this element, eka-tantalum, would therefore consist of the corresponding mass numbers. However, it is possible that EkaTa_{91}^{233} is itself a β -radioactive isotope, so that syntheses to uranium may proceed by the double β -ray transformation :



and the lightest isotope of uranium may therefore be U_{92}^{233} .

† Note added in proof.

Syntheses to uranium would be by the β -radioactivity of the missing isotopes EkaTa₉₁²³⁴ and EkaTa₉₁²³⁶, so that we should expect uranium to consist of the following mass numbers 233, (?) 234, 235, 236, 237, 238, 239 and 240. The next synthesis to the element of atomic number 93 would be by the β -radioactivity of U₉₂²³⁹ and the missing U₉₂²⁴¹. Thus these syntheses did not occur because U₉₂²³⁹ is so unstable by α -ray emission that disintegration occurred rather than synthesis†. The last known element has atomic number 92 because the synthesis link to element 93, eka-rhenium, was so unstable that disintegration to lighter elements always took place. This isotope U₉₂²³⁹, which has been named protactino-uranium, has been shown ‡ to be the probable head of the actinium series.

We conclude that the following isotopes of the radioactive elements would exist if these elements were produced by the synthesis process suggested :—

Atomic number.	Mass numbers.
84	210, 211, 212, 213, 214, 215, 216, 218.
85	217.
86	218, 219, 220, 222.
87	221.
88	222, 223, 224, 226, 228.
89	225, 227.
90	226, 227, 228, 229, 230, 231, 232, 234, 236 (?).
91	233 (?), 235.
92	233 (?), 234, 235, 236, 237, 238, 239, 240.

Though we have accounted for the progressive synthesis of the radioactive elements by this means, it must be remembered that all the isotopes produced are unstable, so that the straightforward process we have assumed will, in general, be complicated by the spontaneous disintegrations proceeding simultaneously. In addition, as a result of the disintegration of the nuclei, it is possible that all four isotopes of an element of odd atomic number may be detected, and perhaps others which are not produced in the general synthesis. It is, moreover, possible that some of the isotopes are connected by disintegration series similar to the three main series.

† Note added in proof.

‡ Walke, *Phil. Mag.* xviii. pp. 259, 262 (1934).

It is significant that many of isotopes suggested to explain the synthesis of the radio-elements have been found † using Allison's magneto-optical apparatus. Bishop ‡ has attempted to construct four radioactive series from the isotopes found, and has indicated that all the lead isotopes may be produced by the disintegration of heavier elements. From the view point expressed in this paper the isotopic constitution of lead is best understood by assuming that normal lead is produced by synthesis, and that radio-genic lead differs from it in containing the end isotopes of several radioactive series.

IX. *Missing Radioactive Series.*

Several of these additional isotopes (which have probably died out) may give rise to radioactive series which are identical with the main series. In fact, it is to be expected that those nuclei formed during the synthesis process as isotopes of the same structure as members of the known series will disintegrate as if they were formed by the decay of the isotope heading the series. For, if the radioactive isotopes were synthesized by neutron addition, many nuclei decayed by α -particle emission before capturing a neutron to become more complex, and if such nuclei decay in a different manner than similar nuclei formed by disintegration of heavier isotopes the problem will be greatly complicated.

On this assumption the main thorium series will be headed by Th_{90}^{232} and Th_{90}^{236} , and the uranium isotopes U_{92}^{240} and U_{92}^{236} , these being connected by the preliminary disintegration



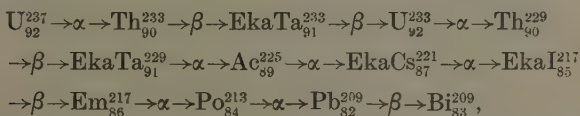
There will be thus three components to the thorium series, as there will be in addition to the disintegration of the main isotope produced by the synthesis process considered, disintegration of the uranium isotopes suggested and Th_{90}^{236} , which are present in only very small abundance if now they exist at all. Thus thorium Th_{90}^{232} , while it is mainly produced by synthesis, is also produced to a slight extent by the disintegration of uranium.

† Phys. Rev. xliii. pp. 48 and 51 (1933).

‡ Phys. Rev. xliii.p. 38 (1933).

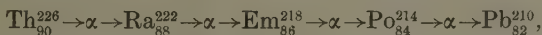
Many of the isotopes of the elements lighter than thorium will have disappeared, as their isotopes have rapidly decayed, but just as some are renewed by the decay of heavier isotopes, so it is possible that the elements 85 and 87 were reproduced in the decay of a short-lived series very similar to the actinium series and headed by U_{92}^{237} and U_{92}^{233} . It is possible, though doubtful, that these isotopes still exist in small abundance, so that this series or part of it may be separated.

It is suggested that this missing series would disintegrate thus,



so that bismuth may be the end product of this missing series. Such a series would explain why Pb_{83}^{209} is still found as a small abundance isotope of lead, since it has been continually renewed from above.

In addition, since the isotopes Em_{86}^{218} , Ra_{88}^{222} , and Th_{90}^{226} are formed by β -ray syntheses, which in each case result in the formation of an α -particle, these isotopes will probably be short lived α -radioactive isotopes, so that a short-lived series headed by Th_{90}^{226} may have occurred during the early synthesis of the radioelements. Thus we have

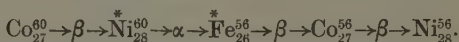


and the lead isotope of mass 210 may be the end product of a short-lived thorium-radium series which has died out.

From these series and the three main radioactive series it is evident that the disintegration of radioactive elements does not necessarily indicate the general trend of nuclear synthesis. During the synthesis of these nuclei neutrons are absorbed and β -radioactivity is the synthesis mechanism, protons and α -particles being formed within the nucleus and not absorbed into from without. During the decay of these elements α -particles are emitted showing that these particles exist within the nucleus as stable units. But the emission of the particles does not show that these units were absorbed by lighter nuclei in stellar synthesis. The recent work

of Fermi has shown the secret of nuclear evolution, and as a result it is certain that the elements were evolved from the simple to the complex. The radioactivity of the heavy elements is due to their instability, and we conclude that these elements were synthesized in the same way as the others and not by any special process. The occasional α -ray emission followed by two β -ray transformations, discussed in section III., to explain the lighter isotopes of tin, xenon, etc., shows, in addition, that there is evidence of series disintegration-synthesis even among the stable elements, and establishes clearly the fact that the radioactive isotopes are in every way similar to normal nuclei except for their instability.

Note added in proof.—Since this paper was sent to press the following confirmatory results have been obtained. Aston has shown that the nickel isotopes of mass number 61 and 62 exist and probably 64 and 56, the latter resulting from the action



He has also detected Cd_{48}^{108} and Cd_{48}^{106} confirming the ideas expressed regarding the isotopic constitution of this element. Evidence of the presence of Co_{27}^{57} has been obtained using Allison's magneto-optical apparatus. Barnes and Gibbs† observed ions from a sample of alkaline sulphates, supposed to contain eka-cæsium of mass 220 ± 1 .

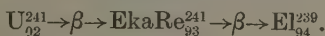
In addition, Fermi found that on subjecting uranium to neutron bombardment induced β radioactivity with four periods of 10 seconds, 40 seconds, 13 minutes, and 1·5 hours was observed. It had previously been shown‡ that the active product of period 13 minutes is not isotopic with any of the elements of atomic number 86 to 92, and it was further demonstrated§ that the active product of period 90 minutes has chemical properties analogous to those of the 13 minutes active product. These activities therefore seem both to be due to products with atomic number higher than 92 and probably to isotopes of the same element.

† Barnes and Gibbs, *Phys. Rev.* xl. p. 318 (1930).

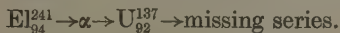
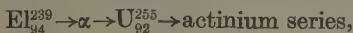
‡ Fermi, 'Nature,' cxxxiii. p. 898 (1934).

§ Fermi, etc., *Proc. Roy. Soc. A*, cxlvi. p. 483 (1934).

The reactions observed suggest the formation of the synthesis links U_{92}^{239} and U_{92}^{241} as a result of neutron capture by the nuclei U_{92}^{238} and U_{92}^{240} . These isotopes cause synthesis to eka-rhenium and element 94 as follows :



These isotopes of element 94 are probably α radioactive (since they would most probably be the lightest isotopes of this element) and thus may be the ultimate sources of the actinium and "missing" series as below :



IV. *The Effect of Longitudinal Strain in the Members of an Elastic Network.* By E. H. BATEMAN, M.A.*

1. **I**T is usual in the determination of deformations and stresses in an elastic network to neglect the effect of the longitudinal strains in the members since the deformation of the network is principally due to flexure, and this approximation has been shown by experimental results to give a reasonable degree of accuracy when applied to simple forms†. The strain energy method may be extended to cover this effect by including, in the expression for the total strain energy, terms representing the strain energy due to direct stresses in the members, but except in a few simple cases the inclusion of these terms would very much complicate and confuse the analysis.

2. As an illustration consider the case of a rectangular portal frame carrying a horizontal load F at the top, as shown in fig. 1. If α , β , δ , η are the terminal couples acting on the bars AB and CD , and if P , Q , and R are the longitudinal forces in the bars AB , BC , and CD ,

* Communicated by the Author.

† F. C. Lea, "The Experimental Determination of the Forces and Moments in the Elements of Indeterminate Structures," *Phil. Mag.* xv. p. 881 (1933).

we shall have the distribution of forces and moments shown in fig. 2, from which it is seen that the forces and moments are connected by the following relations:—

$$\begin{aligned} P &= R, \\ P.d &= \beta + \delta, \\ Q.h &= \delta + \eta, \\ (F - Q).h &= \alpha + \beta, \\ F.h &= \alpha + \beta + \delta + \eta, \\ &= M, \text{ say.} \end{aligned}$$

Fig. 1.

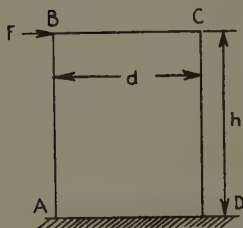
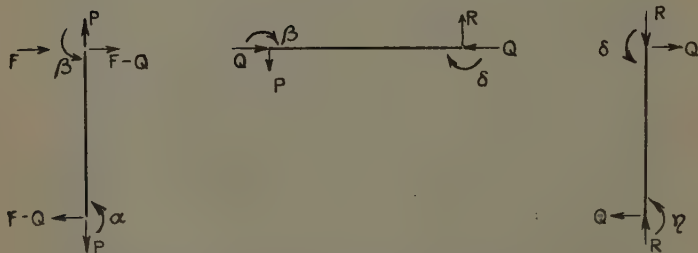


Fig. 2.



Then the strain energy due to the longitudinal forces will be

$$l'P^2 + m'Q^2 + n'R^2$$

where $l' = L/2 E a$, etc., in which L and a are the length and cross-sectional area of the member and E is Young's Modulus.

Then adding the strain energy due to bending *, the total strain energy is

$$W = l(\alpha^2 - \alpha\beta + \beta^2) + m(\beta^2 - \beta\delta + \delta^2) + n(\delta^2 - \delta\eta + \eta^2) + l'P^2 + m'Q^2 + n'R^2,$$

where $l = L/6EI$, etc., in which I is the moment of inertia of the cross-section.

Now writing for P , Q , and R , the values obtained above,

$$W = l(\alpha^2 - \alpha\beta + \beta^2) + m(\beta^2 - \beta\delta + \delta^2) + n(\delta^2 - \delta\eta + \eta^2) + \frac{l' + n'}{d^2} \cdot (\beta + \delta)^2 + \frac{m'}{h^2} (\delta + \eta)^2,$$

and if $r = \frac{l' + n'}{d^2}$, and $s = \frac{m'}{h^2}$,

$$W = l(\alpha^2 - \alpha\beta + \beta^2) + \overline{m + r} \cdot (\beta^2 + \delta^2) - \overline{m - 2r} \cdot \beta\delta + \overline{n + s} \cdot (\delta^2 + \eta^2) - \overline{n - 2s} \cdot \delta\eta.$$

The three equations of minimum strain energy

$$0 = \frac{\partial W}{\partial \beta} = \frac{\partial W}{\partial \delta} = \frac{\partial W}{\partial \eta},$$

can now be written down (since $\frac{\partial \alpha}{\partial \beta} = \frac{\partial \alpha}{\partial \delta} = \frac{\partial \alpha}{\partial \eta} = -1$), thus

$$0 = -3l\alpha + \overline{3l + 2m + 2r} \cdot \beta + \overline{-m + 2r} \cdot \delta,$$

$$0 = -2l\alpha + \overline{l - m + 2r} \cdot \beta + \overline{2m + 2n + 2r + 2s} \cdot \delta + \overline{-n + 2s} \cdot \eta,$$

$$0 = -2l\alpha + \overline{l} \cdot \beta + \overline{-n + 2s} \cdot \delta + \overline{2n + 2s} \cdot \eta,$$

and with the equation,

$$0 = \alpha + \beta + \delta + \eta - M,$$

the values of α , β , δ , η can be determined.

The solution may be written in the form

$$\frac{\alpha}{A} = \frac{\beta}{B} = \frac{\delta}{C} = \frac{\eta}{E} = \frac{1}{\Delta},$$

* E. H. Bateman, "The Strain Energy Method in Elastic Network Analysis," Phil. Mag. xvii, p. 1004 (1934).

where

$$A = M \cdot \{n(2m+n)(3l+m) + mn(n-l) + 2r \cdot n(l+4m+n) + 2s \cdot \{2n(3l+2m) + m(2l+m)\} + 4rs(l+2m+2n)\},$$

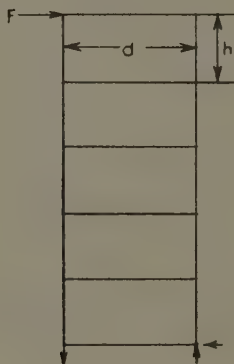
$$B = M \cdot l \cdot \{3n(2m+n) + 2s(6n+2m) + 4rs\},$$

$$C = M \cdot l \cdot \{3n(2m+l) + 2sm - 4rs\},$$

$$D = M \cdot l \cdot \{(2m+l)(3n+m) - m(n-l) + 2r(l+4m+n) - 2sm + 4rs\},$$

$$\Delta = n(2m+n)(6l+m) + l(2m+l)(6n+m) + m(n-l)^2 + 2r(n+l)(l+4m+n) + 2s \cdot \{4n(3l+m) + m(4l+m)\} + 8rs(l+4m+n).$$

Fig. 3.



This solution may be usefully illustrated by a numerical example; thus if $l=m=n$, and $(\kappa/d)=1/20$ where $\kappa=\sqrt{I/a}$, we have $r/l=0.015$, $s/l=0.0075$, and we find the values of α , β , δ , η are $(12.18, 8.98, 8.86, 11.98) \cdot M/42$, respectively, compared with $(12, 9, 9, 12) \cdot M/42$, the values obtained by neglecting the strain energy due to the longitudinal forces.

3. In the case of a network of the type shown in fig. 3, the error due to neglecting the longitudinal forces may be greater. It is not considered worth while to obtain a general solution, since a useful indication of the character of the result can be found by considering the

symmetrical case in which all the vertical members are similar and the horizontal members are also of uniform stiffness. Further, since the characteristic feature of this case is the increase of the forces in the vertical members towards the bottom of the network, the strain in the horizontal members is not taken into account; this is equivalent to writing $s=0$ in the solution for the simple portal and has the effect in that case of making $\alpha=\eta$, and $\beta=\delta$; we deduce a corresponding symmetry of result for the case under discussion, and the number of equations to be solved is reduced by two-thirds.

The vertical members are numbered in sequence from the bottom, thus, 1, 2, 3, . . . , r , . . . , N , and the terminal couples at the lower and upper ends of the r th member are written α_r, β_r ; the longitudinal force in the member is P_r , and the terminal couples acting on the horizontal members are of the form $\beta_r + \alpha_{r+1}$.

Then it may be shown that,

$$l.(\alpha_r + \beta_r) = F.h,$$

$$= m, \text{ say,}$$

and

$$P_N = 2\beta_N,$$

$$P_{N-1} = m + 2\beta_{N-1},$$

$$P_r = m(N-r) + 2\beta_r.$$

The strain energy due to direct stress is $P^2 h / 2Ea$, and due to bending is $(\alpha_r^2 - \alpha_r \beta_r + \beta_r^2) \cdot h / 6EI$, in the r th vertical section, and the part of the total strain energy which depends on the values of α_r, β_r is

$$W_r = 2 \cdot \left\{ \frac{h}{6EI} \cdot (\alpha^2 - \alpha\beta + \beta^2) + \frac{h}{2Ead^2} \cdot (m \cdot \overline{N-r} + 2\beta)^2 \right\}$$

$$+ \frac{d}{6EI'} \cdot (\beta_{r-1} + \alpha)^2 + \frac{d}{6EI'} \cdot (\beta + \alpha_{r+1})^2,$$

or

$$6EK \cdot W_r = 2(\alpha^2 - \alpha\beta + \beta^2) + 2k(m \cdot \overline{N-r} + 2\beta)^2$$

$$+ s(\beta_{r-1} + \alpha)^2 + s(\beta + \alpha_{r+1})^2,$$

where $k = 3I/ad^2$, $s = dI/hI'$, and α, β are written for α_r, β_r .

Hence the equations of minimum strain energy are of the form

$$0 = \frac{\partial W_r}{\partial \alpha_r};$$

thus,

$$0 = 2(2\alpha - \beta + \alpha - 2\beta) + 8k(m \cdot \overline{N-r} + 2\beta) \\ + 2s(\beta_{r-1} + \alpha) - 2s(\beta + \alpha_{r+1}),$$

or

$$0 = 3(\alpha - \beta) - 4k(m \cdot \overline{N-r} + 2\beta) + s(\beta_{r-1} + \alpha - \beta - \alpha_{r+1}).$$

Then writing $\beta = \frac{m}{2} - \alpha$

$$0 = 6\alpha - \frac{3m}{2} - 4k(m \cdot \overline{N-r+1} - 2\alpha) + s(-\alpha_{r-1} + 2\alpha - \alpha_{r+1}), \\ = -\frac{3m}{2} - 4km \cdot \overline{N-r+1} + (6+8k+2s) \cdot \alpha - s(\alpha_{r-1} + \alpha_{r+1}),$$

i. e.,

$$0 = \frac{3m}{2s} + 4 \frac{km}{s} \cdot \overline{N-r+1} + \alpha_{r-1} + \sigma\alpha + \alpha_{r+1},$$

where $\sigma = -2 \left(1 + \frac{3+4k}{s} \right).$

When $r=1$, this equation takes the form

$$0 = \frac{3m}{3s} + \frac{m}{2} + 4 \frac{km}{s} \cdot \overline{N-r+1} + \sigma\alpha_1 + \alpha_2,$$

and thus we have the following system of equations to determine the values of $\alpha_1, \alpha_2, \dots, \alpha_N$:—

$$0 = \frac{3m}{2s} + \frac{m}{2} + 4 \frac{km}{s} \cdot N + \sigma\alpha_1 + \alpha_2,$$

$$0 = \frac{3m}{2s} + 4 \frac{km}{s} \cdot \overline{N-1} + \alpha_1 + \sigma\alpha_2 + \alpha_3,$$

$$0 = \frac{3m}{2s} + 4 \frac{km}{s} \cdot \overline{N-2} + \alpha_2 + \sigma\alpha_3 + \alpha_4,$$

$$\dots \dots \dots$$

$$0 = \frac{3m}{2s} + 4 \frac{km}{s} \cdot 2 + \alpha_{N-2} + \sigma\alpha_{N-1} + \alpha_N,$$

$$0 = \frac{3m}{2s} + 4 \frac{km}{s} + \alpha_{N-1} + \sigma\alpha_N.$$

It is evident that the forces in the members will be

greatest in the bottom panel, and hence the value of α is of the most importance, and we have

$$\frac{\alpha_1}{A} = -\frac{m/2s}{D_N},$$

where

$$D_N = \begin{vmatrix} \sigma, & 1, & 0, & \dots\dots\dots \\ 1, & \sigma, & 1, & \dots\dots\dots \\ 0, & 1, & \sigma, & \dots\dots\dots \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0, & \dots\dots & 1, & \sigma, & 1 \\ N & 0, & \dots\dots & 1, & \sigma \end{vmatrix}.$$

and

$$A = \begin{vmatrix} s+3+8kN, & 1, & 0, & \dots\dots\dots \\ 3+8k(N-1), & \sigma, & 1, & \dots\dots\dots \\ 3+8k(N-2), & 1, & \sigma, & \dots\dots\dots \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 3+8k.2, & \dots\dots & 1, & \sigma, & 1 \\ N & 3+8k, & \dots\dots & 1, & \sigma \end{vmatrix}$$

Then A may be deduced in the form

$$A = 3 \cdot \frac{D_N + D_{N-1} + (-1)^N}{\sigma + 2} + \frac{8k\{N(D_N + D_{N-1}) + D_{N-1}\}}{\sigma + 2} + s \cdot D_{N-1},$$

and we find

$$\alpha_1 = \frac{m}{4(3+4k)} \cdot \left\{ (3+8Nk) - (3-8Nk) \cdot \frac{D_{N-1}}{D_N} - \frac{3(-1)^N}{D_N} \right\}.$$

An estimate of the value of this expression can easily be made, since for most values of σ which have a practical significance, the value of $\frac{D_{N-1}}{D_N}$ is not much

different from $1/\sigma$, and $\frac{1}{D_N}$ is small if $N > 2$. As an illustration take the case in which $N=6$ and the horizontal and vertical members are of the same stiffness;

$$s=1, \sigma=-8, \text{ and } \frac{D_{N-1}}{D_N} = -0.127.$$

Then, when $k=0$,

$$\alpha_1 = 1.127 \times \frac{m}{4},$$

and when $k=0.0075$, corresponding to a value of $1/20$ for (κ/L) ,

$$\alpha_1 = 1.220 \times \frac{m}{4},$$

so that with these values the fact of disregarding the longitudinal forces in the vertical members would introduce an error of about $7\frac{1}{2}$ per cent.

V. *The Relation between Molecular Interaction and the Thermodynamic Properties of Solutions.* By R. P. BELL and O. GATTY †.

Introduction.

THE thermodynamic properties of mixtures are most conveniently expressed in terms of the chemical potential μ of Gibbs. For a mixture containing two components s and r , the chemical potentials are defined by

$$\mu_s = \left(\frac{\partial F}{\partial N_s} \right)_{p, T, N_r}, \quad \mu_r = \left(\frac{\partial F}{\partial N_r} \right)_{p, T, N_s}, \quad \dots \quad (1)$$

where N_s and N_r are the numbers of moles of the two components and F is the function $U + pV - TS$. (Unless otherwise stated, the equations in this paper refer to two component systems, and also to dilute solutions in which $N \ll N_s$.) It is well known that μ can be written in the form

$$\mu_r = \mu_r^0(p, T, s) + RT \log \eta_r + RT \log \pi_r, \quad (2)$$

where η_r is the concentration of the solute, π_r is an activity coefficient becoming unity at infinite dilution, and $\mu_r^0(p, T, s)$ depends on p, T and the nature of the solvent s , but not on the concentration. Experiment usually leads to a measurement of the difference between

† Communicated by the Authors.

the values of μ_r in two systems at the same temperature and pressure. If the systems are denoted by A and B, the above equation gives

$$(\mu_r)_A - (\mu_r)_B = (\mu_r^0)_A - (\mu_r^0)_B + RT \log \frac{(\eta_r)_A}{(\eta_r)_B} + RT \log \frac{(\pi_r)_A}{(\pi_r)_B} \quad (3)$$

If the systems A and B are both dilute solutions in the same solvent, then $(\mu_r^0)_A = (\mu_r^0)_B$ and the ratios $(\eta_r)_A/(\eta_r)_B$ and $(\pi_r)_A/(\pi_r)_B$ are independent of the concentration scale used. If, however, the solvents are not the same, we can obtain from experiment a value for $(\mu_r^0)_A - (\mu_r^0)_B$ which should obviously bear some relation to the interaction of the solute r with the two solvents. It should, however, be emphasized that the numerical value thus obtained depends in general upon the units in which the η_r 's are measured (*e. g.*, mole fractions, volume concentrations, etc.). (If the concentrations are expressed per quantity of solvent, the π_r 's are strictly independent of the concentration scale. If $N_r \ll N_s$, the same is approximately true for any concentration scale.) From the point of view of theories of solution, it is obviously of importance to be able to relate the different values of $(\mu_r^0)_A - (\mu_r^0)_B$ to the molecular fields of force in the two systems.

Although the total value of $(\mu_r^0)_A - (\mu_r^0)_B$ will in general depend on the concentration scale used, it is possible in some cases (at least in principle) to split up the intermolecular forces into a number of different types, and thus to relegate this ambiguity to the contribution of types of force which are not of immediate interest. Thus if we wish to obtain information about the contribution of a particular type of force i to the chemical potential of a solute r in two solvents A and B, we may consider a second solute r^* , differing only from r in the absence of the type of force i . We then have

$$(\mu_r)_A - (\mu_r)_B = (\mu_r^0)_A - (\mu_r^0)_B + RT \log \frac{(\eta_r)_A}{(\eta_r)_B} + RT \log \frac{(\pi_r)_A}{(\pi_r)_B}$$

$$(\mu_r)_A^* - (\mu_r)_B^* = (\mu_r^0)_A^* - (\mu_r^0)_B^* + RT \log \frac{(\eta_r)_A^*}{(\eta_r)_B^*} + RT \log \frac{(\pi_r)_A^*}{(\pi_r)_B^*}$$

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and hence by subtraction,

$$\begin{aligned}
 (\mu_r)_A - (\mu_r)_B - (\mu_r)_A^* + (\mu_r)_B^* &= [(\mu_r^0)_A - (\mu_r^0)_B] \\
 &\quad - [(\mu_r^0)_A^* - (\mu_r^0)_B^*] + RT \log \frac{(\eta_r)_A(\pi_r)_A}{(\eta_r)_A^*(\pi_r)_A^*} - RT \log \frac{(\eta_r)_B(\pi_r)_B}{(\eta_r)_B^*(\pi_r)_B^*} \\
 &\quad \dots \dots (4)
 \end{aligned}$$

The last two terms on the right-hand side of this equation are independent of the concentration scale (in dilute solutions), so that if both $(\mu_r)_A - (\mu_r)_B$ and $(\mu_r)_A^* - (\mu_r)_B^*$ are observable quantities, we can obtain an unambiguous value for the contribution of the forces of the type i to the μ_r^0 's. The separation of the intermolecular fields of force into different parts can in some cases be carried out in practice; *e. g.*, by comparing the partition of K^+ , Cl^- , and argon, or of $N(C_2H_5)_4^+$ and $C(C_2H_5)_4$, Bjerrum† has evaluated the contribution of the ionic fields. In general, however, such a separation is impossible in practice and of doubtful theoretical validity. It is therefore desirable to consider how far it is possible to obtain theoretical expressions for μ_r^* in particular cases, and in particular the case when the state r^* corresponds to a complete absence of interaction in the solution.

The Total Contribution of Intermolecular Forces to the Free Energy of a Mixture. Relation to the Perfect Gas State.

In order to evaluate the total contribution of the intermolecular forces to μ_r , we must compare the actual system with a system of the same composition at the same pressure and temperature, but in which all the intermolecular forces are absent, *i. e.*, the only forces exerted by the molecules of solute or solvent are upon the walls of the vessel. This corresponds to the perfect gas state. In this connexion it is important to note two points. In the first place, the perfect gas state implies not only that molecular attractions are negligible, but also that we may neglect the repulsive forces between the molecules. If as a simplification we are replacing the actual repulsive forces by a rigid molecule of given dimensions, then the

† N. Bjerrum, *Trans. Farad. Soc.* xxiii. p. 445 (1927); *Chemistry at the centenary meeting of the British Association*, p. 34 (1931); N. Bjerrum and E. Jozefowicz, *Z. phys. Chem.* cliv. A, p. 194 (1932).

volume occupied by the molecules themselves must be negligible compared with the total volume of the perfect gas phase. In other words, in a perfect gas there is no restriction as to the distance apart of the centres of two molecules at a given time. In the second place, the transition from the perfect gas state to a liquid state at the same pressure will in general involve large changes in volume.

The chemical potential of a component of a perfect gas mixture is given by

$$[\mu_r]_0 = \mu_r^{00}(T) + RT \log p + RT \log x_r. \quad (5)$$

x_r is the mole fraction $N_r/(N_r + N_s)$, and $\mu_r^{00}(r)$ is a quantity depending only on the temperature. The sign $[\]_0$ indicates that the quantity refers to a perfect gas system. If we write the chemical potential of r in the actual system in the form

$$\mu_r = [\mu_r]_0 + I_r = \mu_r^{00}(T) + RT \log p + RT \log x_r + I_r, \quad (6)$$

this defines the quantity I_r , which we shall term the total contribution of the intermolecular forces to μ_r .

I_s may be defined analogously, and the total free energy of the system is then given by

$$F = N_r \mu_r + N_s \mu_s = N_r [\mu_r]_0 + N_s [\mu_s]_0 + N_r I_r + N_s I_s. \quad (7)$$

If we now write

$$I = N_r I_r + N_s I_s \quad (8)$$

I may be termed the total contribution of the intermolecular forces to the total free energy of the system. I_r , I_s , and I can all be determined experimentally (at least in principle) through vapour-pressure data. It is, however, only for I_r that we can hope in the present state of knowledge to get a theoretical relation to the perfect gas state.

Separation of Solvent-solvent and Solute-solvent Interaction. Relation to non-interacting Solutions.

It should always be possible in principle to calculate I_r from a knowledge of the laws of force between all like and unlike molecules present in the system. This problem is, however, at present insoluble, chiefly because it involves a treatment of the liquid state—*e.g.*, the *a priori* calculation of the volume of a solution in terms of the intermolecular forces. Relation of the whole system to the perfect gas state is thus not of

much practical service, and it is of importance to see whether I_r can be split up into simpler components.

For our present purpose it is of special interest to consider a hypothetical solution in which the fields of force between the solvent molecules are the same as in the actual system, but the solute molecules interact only with the walls of the vessel. We shall term such a system a *non-interacting solution*, and quantities referring to it will be distinguished by the sign $[_z]$. By comparing μ_r in the perfect gas state with μ_r in a non-interacting solution of the same composition at the same temperature and pressure, we can obtain the contribution of the solvent-solute forces to I_r , which we shall denote by $(I_r)_{ss}$. Similarly, by comparing the actual solution with a non-interacting solution of the same composition at the same temperature and pressure, we can obtain $[I_r]_{sr}$ and $[I_r]_{rr}$, which are respectively the contributions of the $s-r$ and the $s-s$ forces to I_r . In infinitely dilute solutions $[I_r]_{rr}$ becomes zero, and in not too concentrated solutions it can be expressed as $RT \log \pi_r$, where π_r is an activity coefficient independent of the concentration scale (*cf.* equation (2)). It is thus possible to arrive at an unambiguous expression for $[I_r]_{sr}$, provided that we can obtain a theoretical expression for μ_r in a non-interacting solution.

By definition, the solute molecules in a non-interacting solution are devoid of any interaction except with the walls of the vessel, and their potential energy is therefore zero throughout the whole volume of the solution, *including* the space occupied by the solvent molecules. The solute may therefore be regarded kinetically as a perfect gas, and its partial pressure is easily seen to be

$$[p_r]_z = \frac{N_r RT}{[V]_z}, \quad \dots \quad (9)$$

where $[V]_z$ is the volume of the solution †.

Well-known arguments with a semi-permeable membrane then give for μ_r in the non-interacting solution

$$[\mu_r]_z = \mu^{00}(T) + RT \log \frac{N_r}{[V]_z} + RT \log RT. \quad \dots \quad (10)$$

† In order that the non-interacting solution shall be homogeneous, it is essential that the external pressure p shall be not less than the sum of the partial pressures of the components, i. e., $p \geq N_r RT/[v]_z + p_s$, where p_s is the vapour-pressure of the pure solvent at p and T . This will always be so provided that the solution is sufficiently dilute.

Comparison of this with (5) gives

$$[I_r]_{ss} = [\mu_r]_z - [\mu_r]_0 = RT \log \frac{N_r + N_s}{[V]_z} - RT \log p + RT \log RT \quad (11)$$

For sufficiently dilute solutions, we can replace $[V]_z$ by V , the volume of the actual solution, and $N_r + N_s$ by N_{ss} , so that (10) and (11) become

$$[\mu_r]_z = \mu^{00}(T) + RT \log \frac{N_r}{V} + RT \log RT. \quad (12)$$

$$[I_r]_{ss} = RT \log \frac{N_s}{V} - RT \log p + RT \log RT. \quad (13)$$

The effect of the $s-s$ forces upon the value of μ_r in dilute solution thus depends only on the molar volume of the liquid solvent, and is independent of the nature or concentration of the solute.

If we now compare the non-interacting solution with the actual solution, we have by definition

$$\mu_r = [\mu_r]_z + [I_r]_{sr} + RT \log \pi_r, \quad (14)$$

and hence from (12)

$$\mu_r = \mu^{00}(T) + RT \log \frac{N_r}{V} + RT \log RT + RT \log \pi_r + [I_r]_{sr}, \quad (15)$$

which gives $[I_r]_{sr}$ in terms of measurable quantities. $N_r/V = c_r$ is the concentration of r expressed in moles per unit volume, so that (15) can be written in the form

$$\mu_r = {}^v\mu_r^0(T, p, s) + RT \log c_r + RT \log \pi_r, \quad (16)$$

where ${}^v\mu_r^0(T, p, s)$, the standard chemical potential on the volume concentration scale † is related to $\mu^{00}(T)$ and $[I_r]_{sr}$ by the equation

$${}^v\mu_r^0(p, T, s) = \mu^{00}(T) + [I_r]_{sr} + RT \log RT. \quad (17)$$

For two solvents A and B, the difference between the ${}^v\mu_r^0(p, T, s)$'s is equal to the difference in the $[I_r]_{sr}$'s, so that equation (3) becomes

$$(\mu_r)_A - (\mu_r)_B = {}^A[I_r]_{sr} - {}^B[I_r]_{sr} + RT \log \frac{(C_r)_A}{(C_r)_B} + RT \log \frac{(\pi_r)_A}{(\pi_r)_B}. \quad (18)$$

† See O. Gatty and A. Macfarlane, *Phil. Mag.* xiii. p. 292 (1932).

We thus see that it is possible by employing the volume concentration scale to obtain an unequivocal measure of the difference between the interactions (at infinite dilution) of a solute molecule with two solvents. This is a result of considerable importance, since a number of attempts have been made to calculate the interaction of a molecule with a solvent on the basis of an idealized model, and there has been considerable doubt as to which concentration scale should be employed in relating such calculations to experimental data. The above treatment makes it clear that the volume concentration scale should be employed.

*Comparison of non-interacting and "perfect" Solutions.
Heat and Volume Changes.*

We have employed the non-interacting solution as a norm to which actual solutions can be referred. A great deal of the thermodynamics of solutions has, however, been based on the concept of "perfect" solutions, and it is of interest to compare the two types of solution. A "perfect" solution is defined by the equation

$$\mu_r = [\mu_r^0]_l(p, T) + RT \log x_r, \quad . \quad . \quad . \quad (19)$$

where $[\mu_r^0]_l$ is the chemical potential of the (actual or hypothetical) pure liquid r at the pressure and temperature considered. The concept of a "perfect" solution thus involves an appeal to the pure liquid state, and hence cannot be assigned any simple kinetic interpretation. In particular it may be noted that if a solute r forms "perfect" solutions with two solvents, the resulting solutions will be in equilibrium with respect to r when its mole fraction is the same in the two phases, while if it forms non-interacting solutions, equilibrium will be attained when the volume concentrations are equal. These two results are not in general equivalent, and it is obvious that the second assumption is simpler from a kinetic point of view. It may further be noted that the "perfect" solution hypothesis gives no direct information about the distribution of a solute between a solution and the vapour phase (except in so far as it relates it to the corresponding distribution in the case of the pure liquid solute).

Attempts which have been made to derive equation (19) on the basis of statistical mechanics † or a simplified

† E. A. Guggenheim, Proc. Roy. Soc. A, cxxxv, p. 181 (1932).

picture of the liquid state † are restricted to the case when the two components have equal molecular volumes, and it is just in this case that the mole fraction and volume concentration scales become equivalent. From the point of view of an analysis of molecular interaction in solution, the "perfect" solution constitutes a very complex problem, and it is certainly preferable to use the non-interacting solution as a standard in problems involving a treatment of forces of interaction in dilute solutions. On the other hand, the "perfect" solution standard is undoubtedly the most convenient for the treatment of purely thermodynamical relations. This is so partly because equation (19) leads to an exactly analogous equation for μ_s , and partly because of the simple nature of the heat and volume relations derived from it. Thus it is well known that the transfer of either component between two "perfect" solutions gives rise to no change in either volume or heat content ‡.

This is not the case for the transfer of solute between two non-interacting solutions. If we have two such dilute solutions in solvents A and B, equation (12) gives

$$^A[\mu_r]_z - ^B[\mu_r]_z = RT \log \frac{(N_r)_A}{V_A} - RT \log \frac{(N_r)_B}{V_B},$$

and hence for the change in partial molal heat content

$$\begin{aligned} ^A[\bar{H}_r]_z - ^B[\bar{H}_r]_z &= -T^2 \left[\frac{\partial}{\partial T} \left\{ \frac{^A[\mu_r]_z - ^B[\mu_r]_z}{T} \right\} \right]_{p, N_r, N_s} \\ &= RT^2 \left(\frac{\partial \log V_A}{\partial T} \right)_p - RT^2 \left(\frac{\partial \log V_B}{\partial T} \right)_p, \quad (20) \end{aligned}$$

where for sufficiently dilute solutions V_A and V_B are the volumes of the pure solvents. If both phases are liquids under a fairly small external pressure, it is unnecessary to distinguish between U and H , and we can also write

$$^A[\bar{U}_r]_z - ^B[\bar{U}_r]_z = RT^2 \left(\frac{\partial \log V_A}{\partial T} \right)_p - RT^2 \left(\frac{\partial \log V_B}{\partial T} \right)_p. \quad (21)$$

† W. Heitler, *Ann. d. Physik*, lxxx. p. 630 (1926).

‡ It should, however, be noted that the laws of "perfect" solutions cannot be deduced from the assumption of zero change in volume and heat content: much more drastic assumptions are necessary. See E. A. Guggenheim, *J. Phys. Chem.* xxxiv. p. 1751 (1930).

If one of the phases is a perfect gas, (5) and (12) give

$${}^A[\bar{H}_r]_z - [\bar{H}_r]_0 = RT^2 \left(\frac{\partial \log V_A}{\partial T} \right)_p - RT. \quad (22)$$

Further, $[\bar{H}_r]_0 = [\bar{U}_r]_0 + RT$, and if again the external pressure is small, ${}^A[\bar{H}_r]_z = {}^A[\bar{U}_r]_z$, so that

$${}^A[U_r]_z - [\bar{U}_r]_0 = RT^2 \left(\frac{\partial \log V_A}{\partial T} \right)_p. \quad (23)$$

It appears at first sight surprising that these energy changes should occur in a system with no interaction between solute and solvent, and it is worth while pointing out their origin. Thus consider the case in which molecules of solute are introduced from a perfect gas into a non-interacting solution. The solution is bounded by a vessel and a piston through which the constant external pressure is applied, both of which are impermeable to solute molecules. The effect of introducing more solute molecules is therefore to increase momentarily the outward pressure upon the piston, and hence to cause the solution to expand slightly until the resultant pressure inside the piston is again equal to the pressure applied externally. For all ordinary values of the external pressure the external work done in this expansion will be negligible: however, energy is also expended against the solvent-solvent attractive forces, and it is this energy which must be compensated by the absorption of heat appearing in equations (22) and (23). It is clear that this heat change (and also the accompanying volume change) will depend upon the properties of the solvent, but not on the nature of the solute. Since the coefficients of expansion of actual liquids range from about 2×10^{-4} to 2×10^{-3} , a gaseous solute forming a non-interacting solution with these liquids would dissolve at constant volume with a heat absorption of about 40–400 calories per mole.

The existence of these heat changes in non-interacting solutions becomes of practical importance in comparing experimental data on heats of transfer with the theoretical values obtained on the basis of any particular molecular model, *e. g.*, a spherical ion in a continuous dielectric. Thus for transfer between any two very dilute solutions (so that the activity coefficients can be taken as unity),

equation (18) gives for the differential heat of transfer at constant pressure

$$\begin{aligned} (H_r)_A - (\bar{H}_r)_B &= -T^2 \left[\frac{\partial}{\partial T} \left\{ \frac{(\mu_r)_A - (\mu_r)_B}{T} \right\} \right]_{p, N_r, N_s} \\ &= -T^2 \left[\frac{\partial}{\partial T} \left\{ \frac{{}^A[I_r]_{sr} - {}^B[I_r]_{sr}}{T} \right\} \right]_p + RT^2 \left(\frac{\partial \log V_A/V_B}{\partial T} \right)_p, \end{aligned} \quad (24)$$

and for the particular case when the phase B is a perfect gas,

$$\begin{aligned} (\bar{H}_r)_A - [H_r]_0 &= -T^2 \left[\frac{\partial}{\partial T} \left\{ \frac{{}^A[I_r]_{sr}}{T} \right\} \right]_p \\ &\quad + RT^2 \left(\frac{\partial \log V_A}{\partial T} \right)_p - RT. \end{aligned} \quad (25)$$

The terms involving the coefficients of expansion of the solvent have been omitted in previous treatments of the Born equation. As shown above, they may amount to several hundred calories per mole and are thus by no means negligible.

In the same way, the partial molal volume of the solute in a non-interacting solution is given by

$$[\bar{V}_r]_z = \left(\frac{\partial [\mu_r]_z}{\partial p} \right)_{T, N_r, N_s} = -RT \left(\frac{\partial \log V_s}{\partial p} \right)_T. \quad (26)$$

The compressibilities of actual liquids range from about 5×10^{-5} to 5×10^{-4} per atmosphere, so that $[\bar{V}_r]_z$ will be of the order of 1-10 c.c. per mole. The transfer of a solute between two non-interacting solutions will thus in general involve a volume change of this order of magnitude. Similarly, for a very dilute solution with interaction, \bar{V}_r is given by

$$\bar{V}_r = \left\{ \frac{\partial [I_r]_{sr}}{\partial p} \right\}_T - RT \left(\frac{\partial \log V_s}{\partial p} \right)_T, \quad (27)$$

where the second term may be at least as important as the first. It should be taken into account in any derivation of volume changes from intermolecular forces, *e. g.*, in treating the electrostriction effect caused by ions.

*Interaction in non-homogeneous Systems.**Relation to Statistical Mechanics.*

For the equilibrium distribution of a given species between a perfect gas phase and a solvent (the solution being so dilute that the activity coefficient can be taken as unity), equation (18) may be written in the form

$$\frac{c}{c_0} = e^{-[I]_{sr}/RT}, \quad . \quad . \quad . \quad . \quad . \quad (28)$$

where c_0 and c are the volume concentrations in the gas and the solvent respectively. This equation bears a close resemblance to what is commonly called Boltzmann's relation, *i. e.*,

$$\frac{c}{c_0} = e^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad (29)$$

where E/N is the potential energy of a solute molecule in the solution, N being Avogadro's number. It therefore seems natural at first sight to identify $[I]_{sr}/N$ with this potential energy. It should, however, be emphasized that (29) is only applicable to a region of *uniform* potential energy, and it is only in this case that $[I]_{sr}/N$ represents an actual potential energy. For the more general case, in which the phase is composed of a number of regions of different potential energy, statistical treatment gives the equation

$$\frac{c}{c_0} = \frac{\sum_i v_i e^{-E_i/RT}}{V}, \quad . \quad . \quad . \quad . \quad . \quad (30)$$

where the i th region has volume v_i and potential energy E_i (with respect to the solute molecule), and $V = \sum_i v_i$ is the total volume of the phase. By comparison with (28)

$$Ve^{-[I]_{sr}/RT} = \sum_i v_i e^{-E_i/RT}. \quad . \quad . \quad . \quad . \quad (31)$$

On the other hand, the mean potential energy of a solute molecule in the phase is defined as

$$\frac{\bar{E}}{N} = \frac{\sum_i E_i v_i e^{-E_i/RT}}{N \sum_i v_i e^{-E_i/RT}}, \quad . \quad . \quad . \quad . \quad (32)$$

which is not in general equal to $[I]_{sr}/N$.

Equation (31) is, of course, related to the general statistical relation between free energy and total energy.

It should, however, be emphasized that the E_i 's in (30), (31), and (32) are potential energies and *not* total energies, *i. e.*, they do not include heat absorbed or emitted by the material constituting the region in question. Thus in (31) and (32), $[I]_{sr}$ and \bar{E} will only satisfy the fundamental thermodynamic relation between free energy and total energy if the v_i 's are independent of temperature, which will not in general be the case. If it were possible to make a complete statistical analysis of the whole system, including the solvent, this distinction would not be necessary, since the heat terms involved would appear as changes in the potential energy and configuration of the solvent molecules. At the moment, however, we are treating the solvent as an auxiliary system, which defines the values of the v_i 's and E_i 's, and heat changes in this system will only be relevant to the chemical potential of the solute in so far as they affect these values. Considerations of this kind apply to any statistical problem in which the parameters defining the system are dependent on the temperature, and Gross and Halpern † have expressed a somewhat similar point of view in connexion with the free energy, electrical energy, and total energy of electrolyte solutions.

Separation of Attractive and Repulsive Forces. Solutions of Limited Interaction. The Concept of Free Space.

If we are idealizing the actual state of a solution by considering the solvent as a continuous medium (as in Born's calculation for ions), then the potential energy of the solute molecule will be uniform throughout the solution. The calculated value of this potential energy can therefore be equated directly to $[I]_{sr}/N$, and the thermodynamic properties of the solution obtained from (15). If we are taking a more detailed view of the system and considering forces between individual solute and solvent molecules, this simple procedure is not possible, and $[I]_{sr}$ must be obtained by averaging in a particular way (corresponding to (31)) over all the possible values of the potential energy.

The mutual potential energy of two molecules at a given distance apart is actually compounded of an attrac-

† P. Gross and O. Halpern, *Phys. Z.* xxvi. p. 403 (1925).

tive and a repulsive potential, both of which vary continuously with the distance. Since, however, the repulsive potential is known to fall off very rapidly with the distance, it is often replaced by the concept of a rigid molecule of fixed dimensions having only an attractive field. This suggests an attempt to separate the contributions of the attractive and repulsive forces to $[I]_{sr}$, and leads to the concept of a hypothetical solution in which the $s-s$ forces are the same as in the actual solution, while the only forces between the solvent and solute molecules are repulsive forces which can be represented by considering the molecules as rigid bodies. We shall term such a solution a *solution of limited interaction*, and quantities referring to it will be distinguished by the sign L . A system of this kind is obviously related to actual solutions much more closely than is a non-interacting solution, and may prove a convenient basis for comparison with experiment.

A total volume V of solvent may be considered as being composed of volume v_1 , which is free space, and volume v_2 , which is occupied by the impenetrable solvent molecules themselves. If we regard these as regions of respectively zero and infinite potential energy with respect to the solute molecules, then equation (31) gives

$$[I]_{sr}^L = -RT \log \frac{v_1}{v_1 + v_2}, \quad \dots \quad (33)$$

and hence from (15)

$$[\mu_r] = \mu_r^{00}(T) + RT \log \frac{N_r}{v_1} + RT \log RT, \quad \dots \quad (34)$$

i. e., the chemical potential is the same as in a non-interacting solution of volume v_1 . Although it is impossible to obtain any exact measure of $(v_1 + v_2)/v_1$, this fraction probably usually has a value of at least 5-10, so that the correction for the volume occupied by the solvent molecules themselves will amount to 1000-1500 calories per mole, and is thus very considerable. The "free space" of a solvent has been commonly allowed for in this form †. Closer investigation, however, shows that considerable caution is necessary in applying (31) (and

† See, e. g., K. Herzfeld, Müller-Pouillet's *Handbuch der Physik*, section on kinetic theory.

hence (33) and (34)) to an actual solution. It is convenient to treat the solute and solvent molecules as spheres of radii R_r and R_s respectively, and to consider separately the cases $R_r \ll R_s$, $R_r > R_s$, and $R_r \approx R_s$.

(a) $R_r \ll R_s$. In this case it is clearly legitimate to consider the solvent as constituting a system divided into two regions of zero and infinite potential energy, and equation (33) may be applied. Except for a heat term of the same nature as in non-interacting solutions (see (20) to (23)), the introduction of solute into a system of this kind involves no change of potential energy. Hence, if we compare the present system with a non-interacting solution of the same composition and total volume, the term $-R \log \frac{v_1}{v_1 + v_2}$ represents a change in positional entropy corresponding to the smaller number of possible arrangements of the solute molecules after the introduction of the repulsive forces. It may be noted that in this case $[I]_{sr}$ depends only on properties of the solvent, *i. e.*, the fraction of "free space."

(b) $R_r > R_s$. In this case it is not allowable to divide the system into two parts with $E=0$ and $E=\infty$: in fact, with respect to the solute molecules the solvent now constitutes a region of *uniform* potential energy. The number of possible arrangements of the solute molecules is obviously the same as in the corresponding non-interacting solution, so that there is no positional entropy term corresponding to (33). $[I]_{sr}/N$ will therefore be equal to the potential energy of a solute molecule in the phase, and this will always have a finite value, since the introduction of a relatively large solute molecule into the system will always involve doing work against the $s-s$ cohesive forces. Since these forces are always short range forces, the work may be conveniently envisaged as "surface energy": if the surface of N solute molecules is σ_r and the surface energy of the solvent is γ_s per unit area, then $[I]_{sr}$ may be written in the form

$$[I]_{sr}^L = \sigma_r \gamma_s \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

Thus in this case $[I]_{sr}$ may be expressed simply as a product of two factors, one depending on the solute and the other on the solvent.

(c) $R_r \approx R_s$. This is the case which corresponds most closely to real solutions, since the molecules of the solvent and solute will in general be of the same order of magnitude. In this case, however, the position is not essentially simplified by considering only repulsive forces between solute and solvent. It is clear from the above discussion that the transition from the corresponding non-interacting state involves both a change in positional entropy and a change in the mutual potential energy of the solvent molecules, but it is no longer possible to express the contribution of either of these factors to $[I]_{gr}$ in the simple forms given above. It may be possible to derive the entropy term by an extension of the method given by Ursell † for a dilute gas of rigid spheres, but the problem appears to be very complicated. The change in the mutual potential energy of the solvent molecules can obviously no longer be expressed in the form (35), since the energy change is only proportional to the surface of the solute molecules when $R_r \gg R_s$.

Although it is thus not in general legitimate to employ the simple free space correction (33), the condition $R_r \ll R_s$ is fulfilled fairly closely by a few actual systems, e. g., solutions of hydrogen or helium in organic solvents, and we shall therefore give the expressions for the heat and volume changes in solutions of limited interaction satisfying this condition. Equation (34) gives

$$[\bar{H}_r]^L - [\bar{H}_r]_0 = RT^2 \left(\frac{\partial \log v_1}{\partial T} \right)_p - RT, \quad . \quad . \quad (36)$$

$$[\bar{V}_r]^L = -RT \left(\frac{\partial \log v_1}{\partial p} \right)_T. \quad . \quad . \quad . \quad (37)$$

On the assumption that v_2 (the volume occupied by the solvent molecules themselves) is independent of p and T , these equations become

$$[\bar{H}_r]^L - [\bar{H}_r]_0 = \frac{v_1 + v_2}{v_1} RT^2 \left(\frac{\partial \log V_s}{\partial T} \right)_p - RT, \quad . \quad (38)$$

$$[\bar{V}_r]^L = -\frac{v_1 + v_2}{v_1} \left(\frac{\partial \log V_s}{\partial p} \right)_T. \quad . \quad . \quad . \quad (39)$$

If, as before, we assume that the free space amounts to 1/10 to 1/5 of the total volume, and that the coefficient of expansion of the solvent is between 2×10^{-4} and 2×10^{-3} ,

† Ursell, Proc. Camb. Phil. Soc. xxiii. p. 685 (1927).

then the right-hand side of (38) gives the by no means negligible values of 200–4000 calories per mole for the heat of solution.

There are no corresponding simple expressions for the cases

$$R_r \gg R_s \quad \text{and} \quad R_r \approx R_s.$$

The Concept of Surface Energy. "Isochemical" Solutes.

As long as $R_r \gg R_s$, the representation of the solute-solvent interaction as surface energy need not be confined to solutions of limited interaction. For the general case in which there are both attractive and repulsive forces between the molecules we can write, in place of (35),

$$[I]_{sr} = \sigma_r \gamma_{sr}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

where γ_{sr} is the energy per unit area of the surface between the solute and the solvent. This equation is not of particular interest when applied to a single solute, since we can make no simple predictions about the value of γ_{sr} . It does, however, lead to results of interest if we consider a number of different solute molecules which differ in size, but are very similar chemically, so that γ_{sr} can be considered to have the same value for all of them in a given solvent. Such a series of molecules has been termed by Brönsted † an *isochemical series*; the best example is a series of colloidal particles of identical composition but different sizes, and the idea can be less rigidly extended to series like the higher normal hydrocarbons. For such a series, $[I_r]_{sr}$ in a given solvent will be proportional to σ_r , which will in turn bear some relation to the molecular weight of the solute: *e. g.*, for spherical molecules $\sigma_r \propto M_r^{2/3}$, while for rod-shaped molecules of constant cross-section $\sigma_r \propto M_r$. It is thus possible to predict certain facts about the thermodynamic properties of an isochemical series: thus for the partition coefficient of any member of the series between two dilute phases A and B, we have

$$RT \log \frac{(c_r)_A}{(c_r)_B} = -\sigma_r (\gamma_{Ar} - \gamma_{Br}), \quad . \quad . \quad . \quad (41)$$

so that from the value of the partition coefficient for one solute it should be possible to predict the partition

† J. N. Brönsted, *Z. phys. Chem. Bodenstein Festband*, p. 257 (1931).
Phil. Mag. S. 7. Vol. 19. No. 124. Jan. 1935. G

coefficients for the remainder of the series. A further application is to the case when different members of an isochemical series are present simultaneously and are interconvertible, *e. g.*, the equilibrium between colloid particles of varying sizes. It can easily be shown that for rod-shaped particles of uniform cross-section the equilibrium number n_M of particles of mass M is given by a relation of the form

$$RT \log n_M = A + BM, \quad . \quad . \quad . \quad (42)$$

while for spherical particles the corresponding relation is

$$RT \log n_M = A + BM + CM^{2/3} \quad . \quad . \quad . \quad (43)$$

A , B , and C being constants.

It should be emphasized that all the considerations of this paragraph apply only to the case when the solute molecules are large compared with those of the solvent, and only to dilute solutions. When this is not so, not only is it difficult to envisage the solute-solvent interaction in terms of surface energy, but there will also be variations in positional entropy, as shown in the preceding paragraph. The application of the concept of surface energy to solutions in general and to more concentrated systems, as in Langmuir's theory of mixtures *, appears to be open to criticism.

VI. Electron Diffraction on Oxide-coated Filaments.

By H. GAERTNER †.

[Plates II. & III.]

Introduction.

RECENTLY there have been published some X-ray investigations on oxide-coated cathodes by Benjamin and Rooksby ‡ and Burgers §. Benjamin and Rooksby made an X-ray analysis of the

* I. Langmuir, Coll. Symp., Monographs (1925), iii. p. 48. Cf. also J. A. V. Butler, Proc. Roy. Soc. A, cxxxv. p. 366 (1932); Butler, D. W. Thomson, and W. H. MacLennan, J. Chem. Soc. p. 674 (1933).

† Communicated by Prof. G. P. Thomson, M.A., F.R.S.

‡ M. Benjamin and H. P. Rooksby, Phil. Mag. xv. p. 810 (1933); xvi. p. 519 (1933).

§ W. G. Burgers. Ztschr. f. Phys. Bd. lxxx. p. 352 (1933).

coating in the activated, flashed, and poisoned states, and got some valuable information about the composition and the character of the coating. Burgers studied the diffusion of BaO and SrO crystals into mixed crystals by heating. One of his conclusions was that the percentage of BaO in the surface layers is diminishing if the heating process of the layer is carried out at higher temperatures than are necessary for the activating process.

To get some information about the topmost surface layers, electrons are more suitable than X-rays; for the electrons have got a small depth of penetration, not more than 10^{-6} cm., and so confine themselves to the surface layers, whereas X-rays give some information about the layer as a whole, as their absorption is only very small.

In the case of oxide-coated cathodes the condition of the surface layers is of special interest. The general assumption is that a monatomic layer of Ba is formed by the activating process on the top of the coating. This layer is supposed to be responsible for the copious stream of electrons which can be drawn from the surface.

It is known that the emission can be fully destroyed by exposure to oxygen for a short time during heating. The same poisoning effect is produced by water-vapour. Benjamin and Rooksby did not find any difference between an X-ray pattern of an activated filament and a poisoned filament, showing that the poisoning only affects the surface layers. They got a further support for this result by the fact that recovery is possible if the surface layer is sputtered off by ions of argon or mercury.

As in principle electrons are a very suitable means in examining surface conditions, it seemed worth while to try whether they would yield some information in this special case. Of course it might have happened that these cathode layers had not given clear patterns owing to various reasons, *e. g.*, charging up, or because the surface of such a coating is too rough for electron diffraction; but it will be seen from the following sections that the use of electron diffraction to examine oxide-coated cathodes is quite promising.

Apparatus.

The apparatus used to take electron diffraction photographs was similar to the one designed by Prof. G. P.

Thomson * for reflexion experiments. The discharge-tube for producing the electron beam was worked with hydrogen entering the discharge-tube through a low-pressure leak.

In order to get an oxide-coated filament a paste consisting of BaCO_3 and SrCO_3 † diluted in water was painted with a glass rod on the flat base of a nickel block. The nickel block had the shape of a half-cylinder with a surface of $7 \times 13 \text{ mm.}^2$. In order to form the carbonates into the oxides the nickel block was heated indirectly by thirteen platinum wires going through the block. The wires were pulled through small quartz tubes for insulation. The lead for the heating current was drawn insulated through a hole bored in the big ground-joint, on which the specimen was fixed. The hole was made airtight by picein. The nickel block reached a temperature of about 1200°K. within a few minutes.

To measure the temperature of the nickel block by a pyrometer a glass window had to be waxed into the back plate of the specimen chamber.

Opposite to the base of the nickel block there was a ground joint in the wall of the apparatus with an insulated anode. The nearest distance between the anode and the movable cathode (the nickel block) was about 8 mm. The rotation of ground-metal joints enabled the nickel block to be moved with 3 degrees of freedom. The emission of the cathode in the activated state was about 10 milliamps./cm.², provided the cathode was in the nearest position to the anode. The voltage for activating was about 50–100 volts. A higher voltage was not suitable owing to a blue glow which developed with it, for the vacuum conditions in this apparatus are not so perfect as in the commercial valves. The apparatus cannot be baked owing to the ground joints and the picein joints. Besides, from the photographic plate some moisture is evaporating permanently.

The gauging of the apparatus was done by taking patterns from cuprite. The structure of cuprite is

* G. P. Thomson and C. G. Fraser, Proc. Roy. Soc. A, cxxviii. p. 661 (1930).

† I have to express my sincere thanks to the Research Laboratories of the General Electric Company, Ltd., Wembley, England, who were kind enough to supply us with a mixture of BaCO_3 and SrCO_3 in equal parts.

known to be a face-centred cube with a cube side $a_w = 4.26 \text{ \AA.U.}$

The patterns were taken with electrons of about 30,000 volts.

The Fresh Layer.

First of all a picture was taken from the fresh layer consisting of a mixture of BaCO_3 and SrCO_3 in equal parts. Barium and strontium carbonates have isomor-

TABLE I.
Mixture of BaCO_3 and SrCO_3 .

Ring.	Intensity.	d (\AA.U.).
1	str.	4.50-4.09
2	f.	3.38-3.14
3	str.	2.84-2.63
4	m.	2.25-1.86
4 <i>a</i>	m.	2.22
4 <i>b</i>	f.	2.07
4 <i>c</i>	m.	1.92
5	m.	1.71-1.61
6	m.	1.51-1.43
7	v.str.	1.34-1.25
8	f.	1.20-1.15
9	f.	1.06-1.02
10	f.	0.97-0.95
11	f.	0.82-0.79

For the intensity the following abbreviations were used :—
str.=strong, m.=medium, f.=faint, v.=very.

phous crystals belonging to the orthorhombic system ; so the mixture should give two similar ring patterns superimposed. For an example see the ring pattern given in Table I. ; fig. 1 (Pl. II.) shows a print from this pattern.

The pattern of fig. 1 (Pl. II.) is rather diffuse. The rings are very broad. Table I. gives only eight broad rings for the interval 1.43-4.50 \AA.U. The diffuseness of this pattern is not accidental. Eleven plates were taken from five different layers, and the diffuseness was always more or less the same.

According to the 'Strukturbericht' by Ewald and Herrmann, p. 325, both patterns belong to the orthorhombic system, space group V_h^{16} . I calculated from the data given in the 'Strukturbericht' the spacings for both structures. In the interval, 1.50–4.51 Å.U., I found ninety-six different spacings for the superimposed patterns.

An X-ray pattern taken from such a layer by the G.E.C. showed sharper lines, whereas an X-ray pattern taken from BaCO_3 by Hüttig and Arbes* was as blurred as mine, with which it agreed fairly well. I mostly ascribe the blurred appearance of the electron patterns to the great number of rings, which belong to the crystals of the orthorhombic type.

As there was no special interest in the initial state of the layer I did not spend any time to improve the patterns taken from fresh layers, in view of the fact that the patterns taken from heated layers are much clearer.

The Activated Layer.

After the investigation of the fresh layer the nickel block on which the paste was painted was heated in the vacuum to form the carbonates into oxides. Fig. 2 (Pl. II.) shows a print taken from a plate which was obtained from an activated layer. The formation process of this layer was done in two stages. At first the layer was heated for 15 minutes at 1200°K. , then a voltage of 54 volts was applied for half an hour, and a current of 2–6 milliamps. was drawn from the layer. The heating current was kept the same all the time.

When the layer was in the nearest position to the anode the emission was 6 milliamps. at 54 volts. The emission of 2 milliamps. corresponds to a greater distance, for the glowing nickel block could not be kept in the nearest position all the time, otherwise the anode got too hot by radiant heat. As has been mentioned already the anode was fixed on a ground joint in the wall of the apparatus. If this ground joint got hot the grease melted away and a leak developed; so I had to change the distance during the formation when the ground joint became too hot.

* G. F. Hüttig and A. Arbes, *Ztschr. f. Anorg. u. allg. Chem.* Bd. cxcvi. p. 408 (1931).

After the formation the layer was allowed to cool down for about 15 minutes before the leak was opened to let hydrogen into the discharge-tube. The picture was taken about half an hour after the end of the formation process. Therefore it can be taken for granted that the layer had reached about room temperature when the picture was taken.

The ring system of fig. 2 (Pl. II.) shows the face-centred cubic structure. All rings are to be seen from

TABLE II.

Spacings belonging to the Activated State.

No.	Intensity.	$\sqrt{\Sigma i^2}$	d (Å.U.).	d calculated from $a_w = 5.12$.
1	str.	$\sqrt{3}$	2.95	2.95
2	m.	$\sqrt{4}$	2.545	2.56
3	str.	$\sqrt{8}$	1.82	1.81
4	str.	$\sqrt{11}$	1.545	1.54
5	f.	$\sqrt{12}$	1.48	1.476
6	f.	$\sqrt{16}$	1.28	1.28
7	str.	$\sqrt{19.5}$	1.15	1.158
8	str.	$\sqrt{24}$	1.04	1.044
9	m.	$\sqrt{27}$	0.981	0.984
10	f.	$\sqrt{32}$	0.904	0.905
11	str.	$\sqrt{35.4}$	0.855	0.86
12	m.	$\sqrt{40}$	0.806	0.81
13	m.	$\sqrt{43.5}$	0.769	0.775
14	m.	$\sqrt{50}$	0.714	0.724

$\sqrt{3}$ up to $\sqrt{50}$. Apart from these rings belonging to the face-centred cubic structure there seems to be only one faint superfluous ring near to the double ring $\sqrt{19}/\sqrt{20}$, about which I have to speak in the next section. The mean values of all spacings d were calculated from six different plates taken from activated filaments. They are given in Table II.

From the values d the length of the cube side was calculated to be

$$a_w = 5.12 \text{ Å.U.}$$

In Table III. I have given the values a_w for each plate separately. There is no difference greater than 0.6 per cent. compared with the mean value: so the agreement is fairly good.

A face-centred cubic structure was to be expected, as both barium and strontium oxides belong to the face-centred cubic system. The lengths of the cube sides of BaO and SrO are 5.53 and 5.15 Å.U. respectively*. Our value 5.12 agrees with the cube side of SrO within the experimental error; hence we can draw the conclusion that the surface layers of our activated filaments mostly consist of SrO.

Furthermore, we have to take into consideration that the intensity scattered by barium is greater than the

TABLE III.

Plate no.	a_w (Å.U.).
7	5.09
56	5.125
57	5.135
70	5.105
71	5.125
72	5.135

intensity scattered by strontium, owing to the higher atomic number of Ba. As we did not find any trace of rings belonging to BaO, we have to conclude that the percentage of BaO in the surface layer of an activated filament is smaller than 10 per cent.

To understand this we have to turn to a paper by A. Claassen and C. F. Veenemans† and the paper by Burgers‡ mentioned above.

Claassen and Veenemans investigated the velocity of evaporation of pure BaO and pure SrO. They found that pure BaO evaporates much more quickly than pure SrO at the same temperature (see Table IV.).

* These values are taken from the 'Strukturbericht' by Ewald and Herrmann.

† A. Claassen and C. F. Veenemans, "Dampfdruckbestimmungen von BaO, SrO, CaO und deren Mischungen aus Verdampfungs- geschwindigkeitsmessungen," *Zeitschr. f. Phys.* lxxx. p. 342 (1933).

‡ W. G. Burgers, *loc. cit.*

The authors made further investigations on mixtures of BaO and SrO. They determined the evaporated quantity of BaO at different temperatures, whereas the evaporated quantities of SrO were too small to be detected.

They noticed that for BaO the velocity of evaporation diminishes with time. This fact is to be expected, for the concentration of BaO in the surface layers is getting smaller and smaller if the loss of BaO by evaporation is greater than the gain by diffusion from the interior. This assumption was supported by the paper of Burgers.

TABLE IV.

(Taken from the paper by Claassen and Veenemans.)

Number of the Molecular Layers evaporating each Minute.

T° K.	BaO.	SrO.
1800	—	(1300)
1700	—	(130)
1600	(2400)	10
1500	360	0.6
1400	42	0.02
1300	4	—
1200	0.2	—

An alteration of the concentration of two components near the surface should be detected by X-ray diffraction patterns taken from the coating.

Burgers concludes that a one-sided blurring of the diffraction rings should occur in this case, whereas the position of the rings would not be altered. for the main intensity is given by crystals in the interior of the coating, where such a variation of the concentration does not occur. He compared the patterns of two filaments which were heated at 1500° K. for 4 and 30 minutes respectively. He noticed that in the second pattern the rings were slightly blurred towards one side. So evidence was obtained that by the heating process the percentage of SrO is growing in the surface layers.

If these investigations are taken into consideration our result seems to be quite natural. Let us assume

that the layer investigated by Burgers had the thickness of 0.1 mm. Then $10^6/5=200,000$ crystal layers have been scattering. If there occurs a noticeable one-sided blurring, as Burgers has found, we have to assume that SrO is predominant, at least in the first 10,000 top-layers; for I do not think that a change of concentration which is confined to less than 5 per cent. of the layers would come out even in X-ray patterns.

In the electron patterns only about twenty topmost surface layers contribute to the scattered intensity. Hence it is not astonishing that for an activated filament there is no trace of BaO to be found in the patterns. At the temperature which is necessary to break down the carbonates and to activate the filaments BaO is evaporating so quickly that only such a small percentage is left in the surface layers that it is not detectable in the electron pattern.

This predominance of SrO in the surface layers, which is to be noticed from the very beginning, will affect deeper and deeper layers the longer the filament has been heated; for Benjamin and Rooksby * mention a filament whose emission had failed after running for several hundred hours at 1100°K . In this case the percentage of BaO and SrO given by the X-ray pattern was 9 per cent. and 91 per cent. respectively throughout the filament. Hence SrO was predominant in the whole layer. These authors got the same results by severe flashing of the filament at 1600°K . After each flash the filament was reactivated. This process of alternate flashing and reactivating was continued until no further reactivation was possible. An X-ray pattern taken from a filament completely flashed always showed only about 9 per cent. BaO left.

All these X-ray results are in agreement with the fact that an electron diffraction pattern shows a great predominance of SrO in the surface of an activated filament from the very beginning.

Layers not sufficiently Heated.

To study the breakdown of the carbonates into the oxides I diminished the time of the heating process. I tried to get the carbonate pattern and the oxide pattern superimposed on one plate. I had found that a heating

* *Loc. cit.*

current of about 2.65 amps. was necessary to break down the carbonates in a short time, so I increased the heating current in five stages according to the following scheme :—

1/2' heating at 1.65 amps.				
1'	„	„	2.00	„
1/2'	„	„	2.25	„
1'	„	„	2.50	„
X'	„	„	2.65	„

Only the heating time of the last stage was altered.

The results obtained from these experiments are as follows :—

1. The change of the carbonates into the oxides is rather abrupt. A heating in the fifth stage at 2.65 amps. for 40 seconds still gave the carbonate structure, whereas a heating for 45 seconds or 1 minute gave the structure of the oxides. The rings of the carbonate structure become a little sharper by the heating process; that might be due to some change in the crystal size produced by the heating. Perhaps the surface is getting smoother through the heating. If the heating process is continued only for a few seconds the pattern is completely changed and shows the face-centred cubic structure of SrO. So the breakdown of the carbonates in the surface layers takes place within a few seconds. Of course nothing can be said about the time which is necessary to break down the carbonates in the interior of the layer. Most probably in the interior the change is not so abrupt as on the surface.

2. In the beginning the oxide structure still shows some superfluous rings, which disappear when the heating process is continued sufficiently long. The intensity of these rings is very small. By a careful examination of all the plates which give the ring pattern of SrO I found six rings which did not fit the structure of SrO. Table V. gives these rings, with the position in the pattern and the corresponding spacings.

Apart from ring (*d*), which was only found in patterns from non-activated layers, the rings were found both from layers which were only heated and from layers which were activated as well.

The rings (*b*), (*c*), (*f*), and perhaps (*e*) can be ascribed to BaO, corresponding to $\sqrt{8}$, $\sqrt{11}$, $\sqrt{24}$, and $\sqrt{19.5}$ respectively. Ring (*a*) belongs to BaCO₃; the same might hold for rings (*d*) and (*e*). I may mention that ring (*d*) has the same spacing as a ring which appears in the poisoned films, which are dealt with in one of the following sections; so ring (*d*) may belong to the hexagonal pattern (see next section).

The possibility remains that the spacings (*b*), (*d*), (*e*), and (*f*) correspond to the rings $\sqrt{6}$, $\sqrt{17}$, $\sqrt{18}$, and $\sqrt{20}$ of Ba; but under our experimental conditions it is rather improbable that Ba occurs in bulk on the

TABLE V.
Superfluous Rings in the SrO Structure.

	Position in the pattern.	Spacing (Å.U.).
<i>a</i>	above $\sqrt{4}$	2.22 ± 0.03
<i>b</i>	below $\sqrt{8}$	$1.97 - 2.01$
<i>c</i>	between $\sqrt{8}$ and $\sqrt{11}$	$1.69 - 1.73$
<i>d</i>	below $\sqrt{16}$	1.38 ± 0.025
<i>e</i>	below $\sqrt{19.5}$	1.19 ± 0.01
<i>f</i>	between $\sqrt{19.5}$ and $\sqrt{24}$	$1.12 - 1.13$

surface to give such rings, especially as some of the rings were obtained from layers which had been heated without any electrolysis. So it seems to be more justifiable to attribute the spacings to BaO and BaCO₃. Fig. 3 (Pl. II.) gives a print from a plate taken from a layer which was only heated; it shows the rings (*a*), (*d*), (*e*).

3. The third observation made on layers which were not fully heated was the following:—If the taps were closed intentionally during the heating process the evaporated CO₂ was not pumped out. The layers were then formed in this atmosphere of CO₂. In this case the only difference was that it took a longer time to break down the carbonates. On one pattern I still got the carbonate structure after $1\frac{1}{2}$ minutes heating in the fifth stage, whereas the breakdown occurred after 45 seconds if the CO₂ was pumped out.

This result was to be expected, as the breakdown

of the carbonates by heating is a dynamic equilibrium, so that a reformation of the carbonates takes place if sufficient CO_2 is present.

Originally these experiments were not made to study this equilibrium, but to see whether a hexagonal structure, which was found sometimes, had something to do with the presence of CO_2 during the forming process. It followed from these experiments that the presence of CO_2 really does not produce this hexagonal structure, which is treated in the next section.

The Hexagonal Structure.

A good number of plates show a ring pattern which fits the Hull curves of the hexagonal system. The structure was found on a fairly great number of plates (see fig. 4 (Pl. II.), which shows a print from plate 50).

Table VI. gives the spacings calculated from the plates 28, 45, 47, 49, 50, 55, 69; the intensity is given as well. The ninth column gives the mean values of the spacings, and the tenth column the Miller indices h, k, l . The last column gives the lattice constant a , which has been calculated according to the formula

$$\frac{1}{d^2} = \frac{1}{a^2} \left[\frac{4}{3} (h^2 + k^2 + hk) + \frac{a^2}{c^2} l^2 \right],$$

using the value

$$\frac{c}{a} = 1.25 \text{ taken from the Hull curves.}$$

The mean values of the lattice constants are

$$a = 3.675 \text{ \AA.U., and}$$

$$c = 4.575 \text{ \AA.U.}$$

Most of the different values for a agree within 1 per cent., which is as good as can be expected; so our conclusion that the ring pattern belongs to the hexagonal type seems to be rather probable.

The rings 4, 6, 12, and 15 do not fit with the hexagonal type. The corresponding spacings are:—

$$d = 1.98 \text{ \AA.U.}$$

$$d = 1.77 \text{ \AA.U.}$$

$$d = 1.25 \text{ \AA.U.}$$

$$d = 1.01 \text{ \AA.U.}$$

Ring 4 was found three times, ring 6 only once.

TABLE VI.
Belonging to the Hexagonal Structure.

	28.	45.	47.	49.	50.	55.	69.	Mean values.	<i>h. k. l.</i>	<i>a.</i>
1.....	—	—	—	—	3.20 str.	3.18 str.	3.22	3.20 str.	1 0 0	3.69
2.....	—	—	2.60 str.	—	2.685 str.	2.63 f.	2.68	2.65 str.	1 0 1	3.72
3.....	2.24 str.	2.29 str.	1.97 f.	2.245 str.	2.31 str.	2.26 str.	2.28	2.275 str.	0 0 2	3.64
4.....	—	—	1.86 str.	1.975 f.	1.99 f.	—	—	1.98 f.	—	—
5.....	1.81 str.	1.88 str.	1.86 str.	1.84 str.	1.86 str.	1.87 str.	1.84	1.85 str.	{ 1 0 2	3.65
6.....	—	—	—	1.77 f.	—	—	—	1.77 f.	{ 1 1 0	3.70
7.....	1.565 f.	1.59 m	1.59 m.	1.58 m.	1.58 m.	1.59 m.	1.58	1.58 m.	2 0 0	3.65
8.....	—	—	1.51 f.	—	1.497 f.	—	—	1.505 f.	2 0 1	3.68
9.....	—	—	1.45 m.	1.44 m.	1.425 m.	1.40 f.	1.44	1.44 m.	1 1 2	3.685
10.....	1.38 str.	1.395 m.	1.38 f.	1.375 m.	1.39 f.	—	—	1.384 m.	1 0 3	3.68
11.....	—	—	1.31 m.	1.31 m.	1.305 m.	—	—	1.31 m.	2 0 2	3.68
12.....	1.24 str.	1.26 m.	1.235 f.	1.247 m.	—	1.257 f.	1.26	1.25 m.	—	—
13.....	1.14 str.	1.17 str.	1.165 str.	1.15 str.	1.167 str.	1.174 str.	1.14	1.16 str.	1 2 1	3.66
14.....	1.067	1.075 str.	1.06 str.	1.06 str.	1.054 str.	1.06 str.	1.05	1.06 str.	{ 3 0 0	3.68
15.....	1.01 f.	1.015 f.	1.01 f.	1.013	0.988 f.	—	—	1.01 f.	{ 1 0 4	3.61
16.....	0.957 f.	—	0.958 f.	0.955	—	—	—	1.01 f.	{ 1 2 2	3.67
17.....	0.917 f.	0.917 f.	0.920 f.	0.913 f.	—	—	—	0.956 f.	{ 1 1 4	3.62
18.....	0.853 m.	0.871 str.	0.862 str.	0.851 str.	0.862 str.	0.867 str.	0.847	0.859 str.	{ 3 0 2	3.66
19.....	0.81 f.	0.816 m.	—	0.807	0.810 m.	—	—	0.811 m.	{ 2 0 4	3.62
20.....	0.769 f.	0.781 m.	—	0.77	0.77 m.	—	—	0.770 m.	—	—
21.....	—	0.724 m.	—	—	—	—	—	0.724 m.	—	—

It is not impossible that the rings (b) and (c) (see Table V.) have got the same origin as rings 4 and 6 of Table VI.

The hexagonal type was found unexpectedly. Although the type appeared quite often I did not have time enough to find out the conditions under which it could be produced intentionally. I did not find the type on the last thirty plates of my investigation. From plate 70 on I took more care about the vacuum than I did before. The test of the vacuum was done in the following way :— After some time of pumping all the taps of the apparatus were closed and the high voltage was put on the discharge-tube. When no flashing occurred in the tube for about $1\frac{1}{2}$ minutes, the vacuum was regarded as sufficient. After such a test I never was able to find the hexagonal structure, so the development of this type might depend on the vacuum. The last pictures of this type were found when the taps were partly blocked by tap-grease ; but I could not find the real reason for the appearance of this pattern, as the formation in oxygen or air at a pressure of 0.1 mm. Hg. produces a pattern in which the structure of SrO is predominant. If the forming takes place in the atmosphere of the evaporated CO_2 this structure does not appear either, but the carbonate pattern persists longer, as I pointed out in the end of the last section.

Some experiments were made on poisoned layers, which are described in the following section (see p. 96). Poisoning means that the layers were formed to give emission, and after electrons had been drawn for some time suddenly some oxygen was let into the apparatus. The emission immediately dropped to zero. Unfortunately the patterns taken from these layers did not allow any definite statements, but the possibility remains that this hexagonal structure is due to some poisoning effect (see next section).

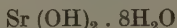
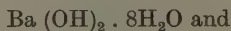
This is in agreement with the fact that the emission from these layers with a hexagonal structure generally was rather poor. Some of the layers had only been heated without drawing electrons, but if an activation was tried the emission varied for the different layers from

0.1–2.5 $\frac{\text{milliamps.}}{\text{cm.}^2}$, whereas the emission of a fully

formed layer was about $\frac{10 \text{ milliamps.}}{\text{cm.}^2}$. The only

exception is plate 50, which gave 8.5 milliamps. in spite of a hexagonal structure; so the most probable conclusion is that the layers with a hexagonal pattern have got a poor emission owing to some poisoning effect due to bad vacuum conditions.

The structure cannot be the usual hydroxide, for



belong to the tetragonal system, and I could not find a correspondence to the structures of $\text{Sr (OH)}_2 \cdot 1\text{H}_2\text{O}$, Sr (OH)_2 , $\text{Ba (OH)}_2 \cdot 1\text{H}_2\text{O}$, Ba (OH)_2 , given by Hüttig and Arbes*; but apart from the poisoned state some SrO may be present at the same time, as several rings of Table VI. fit the structures of SrO . It must be left to some further investigations to find out definitely the origin of this hexagonal type.

Oxygen Poisoning.

Benjamin and Rooksby† made some investigations on filaments poisoned with oxygen. After activation oxygen at a pressure of 0.01 mm. Hg was admitted to contact with the filament, which was maintained at its normal operating temperature. The emission immediately fell to zero; but the X-ray photograph revealed no sensible difference in coating composition from that of the activated filaments.

In my experiments on poisoned layers I always took a pattern from the formed layer before I started to poison it. The first series of plates taken from each layer was done without any poisoning. When the apparatus had been pumped out again the layer was always re-heated and re-formed.

In this series I noticed that the contact with the air did not produce a permanent change in the structure. A fully formed layer which gave the structure of SrO on the first plate still showed this pattern on the following plates. The emission of the layer could always be brought to the same value, only the rings became blurred in time; but if the layer was not fully formed in the beginning,

* G. F. Hüttig and A. Arbes, *Zeitschr. f. anorg. u. allg. Chemie*, cxii. p. 230 (1930); cxvi. p. 408 (1931).

† *Loc. cit.*

or was poisoned with oxygen in the meantime, then the different patterns taken from the layer showed some differences.

The relative intensity of the rings did not remain constant in this case. One ring especially, belonging to the spacing of about $d=1.35$ Å.U., could be strong on one plate and hardly to be seen on the next one. When the ring was strong the ring pattern resembled the patterns of the hexagonal structure. Unfortunately it could not be detected whether the rings $d=3.20$, $d=2.65$, and $d=2.275$ Å.U., which are also characteristic of the hexagonal pattern, were on the plates taken from poisoned layers, for the primary spot extended too far. Apart from ring $d=1.35$ Å.U. almost all the rings belonging to poisoned films also fitted the structure of SrO, as do most of the outer rings of the hexagonal patterns (see Table VI.). So when the ring was missing the pattern was like that of SrO.

On plate 28 I got a strong ring $d=1.38$ Å.U. from a layer which was only heated but not formed. The structure is hexagonal (see Table VI.). After having taken the picture I tried to activate the layer before I let air into the apparatus. I only reached an emission of 2.5 milliamps. After pumping out again I brought the emission up to 5.5 milliamps. Plate 29 taken from it was underexposed, but also seems to have a hexagonal structure.

By re-forming for the second time the emission rose to 8.5 milliamps. Plate 30 taken from the layer shows the SrO pattern in agreement with the higher emission obtained. The ring $d=1.38$ Å.U. is not present any longer. Before a new plate was put in the layer was poisoned with oxygen. After pumping out again the layer was re-heated, but no emission obtained, showing that the layer was still in a poisoned state. A strong ring $d=1.37$ Å.U. reappeared on plate 31, together with a faint ring $d=1.25$ Å.U., equally found on plate 28. The rest of plate 31 was in agreement with the SrO structure.

Before a second plate 32 was taken from this poisoned layer it was re-heated, but still did not give any emission. Plate 32 showed the same pattern as plate 31.

Both rings disappeared when the activation of the layer was better, and reappeared after the poisoning.

Hence they might be taken as a signal for some change in the surface due to some poisoning effect. As the patterns taken from poisoned films have only such rings as are found in the hexagonal structure as well, there seems to be a connexion between them, as has been suggested for some other reasons in the last section.

My experiments on poisoned layers were carried out at an early stage of the investigation. By taking a pattern from the formed layer before poisoning it I was forced to bring the layer into contact with the air when I took out the first plate. Unfortunately during the later stage of my investigation the layer always came off the base, when the air was streaming into the apparatus. Hence later on I never succeeded in taking two pictures from the same layer. I do not know the reason why this did not happen in the beginning. I changed the roughness of the surface, to see whether the layer would stick better on a rough surface, I changed the thickness of the layer, but everything was in vain.

As I did not have much time to spend on this phenomenon I could not find out the reason; but we must conclude that we have to avoid the layer getting into contact with the air before the poisoning process starts. To prevent this it would be suitable to use a multiplate camera, as has been devised by Trendelenburg and Wieland *. Finally, I will mention that by running the formed layer in oxygen the surface gets rather rough; so it is difficult to get a clear pattern. Especially the rings near to the primary spot disappear in the blackening, and the determination of the structure becomes difficult.

The Tetragonal Structure.

A tetragonal structure was found on the plates 34 and 65. Fig. 5 (Pl. III.) shows a print taken from plate 34.

This structure, which consists of a great number of sharp rings, appeared quite unexpectedly. Before the layers were painted on the nickel body the apparatus had been standing open for some days in both cases; so it is possible that some moisture from the air was still present when the layers were heated, for the layers were completely poisoned. No emission could be obtained.

* F. Trendelenburg and O. Wieland, *Wissenschaftl. Veröffentlichungen aus dem Siemens Konzern.* xiii. Bd. p. 42 (1934).

The structure was determined by the Hull curves, which gave the ratio : $\frac{c}{a} = 0.9$.

According to the formula

$$a^2 = d^2(h^2 + k^2 + \frac{a^2}{c^2} \cdot l^2),$$

the mean values of the lattice constants were calculated to be

$$a = 6.46 \text{ \AA.U.},$$

$$c = 5.82 \text{ \AA.U.}$$

The rings (0 0 2) and (4 0 0) are missing. On plate 34 the ring (2 0 0) seems to be double, which might be due to the missing ring (0 0 2). The faint rings nos. 3, 6, and 13 do not belong to the tetragonal structure. The corresponding spacings are

$$d = 2.395 \text{ \AA.U.},$$

$$d = 1.995 \text{ \AA.U.},$$

$$d = 1.18 \text{ \AA.U.}$$

Apart from this the agreement is so good that the determination of this structure is fairly certain. Most probably this structure belongs to some hydroxide form. Natta* has found $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ to belong to the tetragonal type and having the lattice constants

$$a = 6.41 \text{ \AA.U.},$$

$$c = 5.807 \text{ \AA.U.},$$

$$\frac{c}{a} = 0.906.$$

These values agree with our result very well. According to Bauer† $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ are isomorphous; but I did not find anything about the lattice constants of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. Hence a comparison is not possible, but it might be the case that the scattered intensity is partly due to the Ba compound, especially as barium-hydroxide is formed by heating BaCO_3 in water-vapour. Of course the octahydrate will only be found in the surface layers, as certainly there was not moisture enough for the whole layer. Our

* Natta, *Gazz.* lviii. p. 870 (1928) (see 'Strukturbericht,' p. 776).

† O. Bauer, *Ztschr. f. anorg. Chemie*, xlvii. p. 418 (1905).

determination is in agreement with the poisoned state of the layer, for it is known that oxide-coated cathodes can be poisoned by moisture.

Patterns taken from the Nickel Base.

Towards the end of my investigation I took a plate from the nickel base. The base was rubbed with rather coarse emery paper no. 0. After rubbing I cleaned the surface with tissue-paper dipped into alcohol.

From the surface treated in this way I got the pattern given in fig. 6 (Pl. III.). Only two blurred rings are to be seen. The corresponding spacings are 2.30 Å.U. and 1.31 Å.U.

The structure of nickel is a face-centred cube with a cube side 3.52 Å.U. The greatest possible spacing corresponding to the $\sqrt{3}$ ring is $\frac{3.52}{\sqrt{3}} = 2.03$ Å.U., whereas

the spacings belonging to the $\sqrt{8}$ and $\sqrt{11}$ rings are 1.24 and 1.06 Å.U. respectively; so the agreement is not very good. The spacing of the first ring is bigger than should be expected from the ordinary crystal. Therefore I am inclined to assume that these two rings correspond to the two smudgy rings of a Beilby layer found by French * on polished metals.

After having pumped out again I heated the nickel block in the usual way. In the beginning of the heating process there may have been an air pressure of 0.01 mm. Hg. I kept the block glowing at about 1200° K. for 17 minutes. The pump was pumping all the time, so that the vacuum was improving during the heating process. A new picture taken from this heated base in the cold state is given in fig. 7 (Pl. III.).

Instead of the two blurred rings a number of fairly sharp rings is to be seen (see Table VII.). The rings nos. 2, 3, 6, 7, 9, 10, 11, 12, 13 of this table fit the structure of NiO very well. NiO has a face-centred cube with a cube side $a_0 = 4.17$ Å.U.

The rings 1, 4, 5, 8 of Table VII. were attributed to the rings $\sqrt{2}$, $\sqrt{5}$, $\sqrt{6}$, and $\sqrt{14}$ of NiO; but the difficulty is that these rings are forbidden in an ordinary face-centred structure.

* R. C. French, Proc. Roy. Soc. A, cxi, p. 637 (1933).

A possible explanation for the appearance of these rings is given by the fact that the heating process took place under low air pressure, so there was not enough oxygen present to oxidize all nickel atoms in the surface layers. Many nickel atoms were left without an oxygen partner; hence the lattice of the formed NiO crystals contains more Ni ions than oxygen ions.

In an ordinary face-centred cube the adjacent (1 1 0) planes, for instance, contain as many oxygen ions as

TABLE VII.

Nickel Body heated in the Apparatus at an
Air Pressure of 10^{-2} – 10^{-3} mm. Hg.

Ring.	Intensity.	d (Å.U.).	$\sqrt{\Sigma i^2}$.	α_w .
1	v.str.	2.96	$\sqrt{2}$	4.19
2	str.	2.43	$\sqrt{3}$	4.21
3	str.	2.09	$\sqrt{4}$	4.18
4	f.	1.88	$\sqrt{5}$	4.20
5	f.	1.69	$\sqrt{6}$	4.14
6	str.	1.49	$\sqrt{8}$	4.21
7	str.	1.25	$\sqrt{11.3}$	4.20
8	f.	1.11	$\sqrt{14}$	4.17
9	f.	1.045	$\sqrt{16}$	4.18
10	str.	0.949	$\sqrt{19.5}$	4.20
11	str.	0.851	$\sqrt{24}$	4.17
12	f.	0.795	$\sqrt{27}$	4.13
13	m.	0.697	$\sqrt{35.4}$	4.15

Mean value of α_w = 4.18 Å.U.

Theoretical value of α_w = 4.17 Å.U.

nickel ions; so their scattering power is equal, and the waves scattered by them are cancelled. So the $\sqrt{2}$ ring is missing; but if the nickel ions which replace the missing oxygen ions are spread irregularly in the lattice two adjacent (1 1 0) planes have got a different scattering power, especially as the scattering power of nickel is much greater than that of the replaced oxygen. Besides, according to this assumption the concentration of the oxygen ions in the surface layers will be diminishing towards deeper layers. Owing to these irregularities

some rings which are forbidden for ordinary NiO come into existence. This seems to be the most natural explanation which can be given for the appearance of the rings $\sqrt{2}$, $\sqrt{5}$, $\sqrt{6}$, and $\sqrt{14}$ in the pattern taken from the oxidized nickel base.

Some Suggestions for Future Experiments.

In the case of the paste-cathodes only about 0.1 per cent. of the surface is covered with small areas consisting of barium, according to Espe* ; hence, apart from the roughness of such a layer, it is highly improbable that such a small percentage should be seen in the diffraction pattern. But in the case of the cathodes formed by heating barium-azide and evaporating Ba on the surface of oxidized tungsten the whole area is covered by a monatomic layer of emitting Ba. Therefore a plate taken from such a cathode really might yield some information about this interesting layer.

Summary.

1. By means of electron diffraction the surfaces of oxide-coated cathodes were examined. The cathodes were formed from a paste consisting of BaCO_3 and SrCO_3 painted on the flat base of a nickel block.

2. The fresh layer gave a Debye-Scherrer pattern which was rather diffuse.

3. The activated layer gave much sharper rings with the structure of SrO, showing that in the activated state the percentage of SrO in the surface layers amounts to at least 90 per cent.

4. If the heating process is interrupted before the activation is finished some superfluous rings are to be found, which can be attributed partly to the carbonate structure of the initial state, partly to BaO.

5. Although some of these superfluous rings could be attributed to Ba, such an attribution is fairly improbable (see last section).

6. When the vacuum was not perfect sometimes a hexagonal structure appeared. The reason for the appearance of this structure is not quite clear. Probably it is due to some poisoning effect, as a connexion was found with patterns taken from layers which were

* W. Espe, *Ztschr. f. techn. Physik*, Bd. x. p. 489 (1929).

poisoned intentionally; but owing to some difficulties in taking patterns from poisoned layers nothing definite about this can be said yet.

7. A tetragonal structure found on two plates unexpectedly was attributed to hydroxide compounds in agreement with the fact that the layers which showed this structure did not give any emission.

8. A pattern taken from the nickel base, which was heated in the apparatus under low air pressure, showed some forbidden rings in the NiO pattern. These rings were explained by the assumption that in the NiO lattice nickel ions replaced some of the oxygen ions, which are missing, because the oxidation took place under low pressure. This irregularity is supposed to produce the forbidden rings.

I wish to express my sincere thanks to Prof. G. P. Thomson, who proposed the subject of this investigation and who gave many valuable suggestions. I am indebted to the Deutscher Akademischer Austauschdienst for a scholarship, during the tenure of which this work has been carried out. Finally, I have to thank Dr. Trendelenburg and Mr. E. Franz for taking prints from the plates according to their "Sektorkopierverfahren" *.

Berlin-Siemensstadt.

June 18th, 1934.

VII. *Beat Notes, Combinational Tones, and Sidebands.*

By HERBERT HAZEL, Ph.D. (*Indiana University, Bloomington, Indiana*) †. (Submitted in partial fulfillment of the requirements for the Ph.D. Degree at Indiana University.)

Helmholtz-Koenig Controversy.

WITH the publication in 1870 of the third edition of Helmholtz's "Tonempfindungen," a controversy was started between Helmholtz and Koenig, the two outstanding acousticians of the time, concerning the objective reality of combinational tones. Helmholtz maintained that combinational tones produced by his

* F. Trendelenburg and E. Franz, *Wissenschaftliche Veröffentlichungen aus dem Siemens Konzern*, Bd. xiii, p. 48 (1934).

† Communicated by the Author.

double siren could be detected by means of tuned resonators *.

Koenig disputed Helmholtz's statement that combinational tones cause response in tuned resonators, and challenged the view that these tones exist external to the ear †. Lord Rayleigh ‡, Waetzmann, Edser and Rucker § supported Helmholtz with experimental and theoretical evidence, while Preyer || and Bosanquet ¶ joined Koenig in his dissention.

Sideband Controversy.

In the development of radio communication the question of combinational frequencies, and particularly the question of their objective existence, was revived again in the form of the sideband discussion. Curiously enough, no one seemed to recognize the connexion with the combinational tone question which had been argued for more than fifty years.

It can be shown mathematically that when a radio carrier wave is modulated, a band of frequencies is produced on either side of the carrier. Each frequency present in the modulating wave gives rise to two derived frequencies when it is combined with the carrier. In America radio engineers generally accepted the existence of these sidebands without question. In England quite a debate was stirred up on the physical significance of the sideband equations. Between 1928 and 1931 many arguments were advanced by disagreeing groups **. The debaters included such eminent radio authorities as Sir Ambrose Fleming, G. W. O. Howe, F. M. Colebrook, E. B. Moullin, and J. Robinson.

The sideband question, like the combinational tone controversy, gradually subsided with conflicting views still prevailing.

* Helmholtz, 'Sensations of Tone' (Ellis's translation), pp. 152-205, 527-538.

† Koenig, "Ueber den Zusammenklang Zweier Töne," *Pogg. Anal.*, Feb. 1876.

‡ Lord Rayleigh, 'Theory of Sound,' vol. ii. p. 460.

§ Rucker and Edser, *Phil. Mag.* vol. xxxix. p. 341 (1895).

|| Preyer, 'Akustische Untersuchungen,' published in Jena, 1879.

¶ Bosanquet, "On the Beats of Consonances of the Form $h:l$," *Proceedings of the Physical Society of London*, May 1881.

** 'Experimental Wireless and Wireless Engineer': August, November, December, 1928; January, February, 1929; March, 1930; January, May, June, August, 1931.

Frequency and Harmonic Analysis.

Complex disturbances, such as waves of varying amplitude, cannot be described in terms of a single frequency.

A periodic disturbance of any wave form can be analysed, however, into components of sinusoidal character. By Fourier's theorem we can expand a function, $f(x)$, into a series as follows :—

$$f(x) = b_0/2 + b_1 \cos x + b_2 \cos 2x + b_3 \cos 3x + \dots + \\ a_1 \sin x + a_2 \sin 2x + a_3 \sin 3x + \dots$$

Now when $f(x)$ is specified, the coefficients of the sine and cosine terms in the series are unique. A given wave form can be analysed harmonically, then, into one and only one definite set of sinusoidal components. There is no reason, however, why a given wave form might not be analysed into another set of components having non-sinusoidal form.

Our custom of expressing periodic disturbances in the form of trigonometric functions, along with our experimental use of tuned selective circuits in wave analysis, has warped our definitions to fit that mode of representation. Experimental analysis of a non-sinusoidal disturbance with a wave-metre circuit gives the sinusoidal components of the disturbance. One might hastily conclude that all periodic disturbances are fundamentally sinusoidal in character, but the apparent warping into this form is due to the fact that wave-metre circuits used in the analysis undergo natural oscillations of nearly sinusoidal character. Periodic disturbances expressed in trigonometric form or analysed experimentally with wave-metre circuits have a single definite frequency only if the disturbance is sinusoidal in form. It should be emphasized that the frequency of a non-sinusoidal disturbance need not be variable if it is expressed in suitable non-sinusoidal form. But any attempt to express such a disturbance in trigonometric form must inevitably result in more than one frequency, just as experimental analysis with a tuned wave-metre circuit always gives the several sinusoidal components of the original disturbance.

Response to a Disturbance.

The response excited in a body by any disturbance incident upon it depends upon the nature of the disturbance and upon the character of the responding body. For a linear body—that is, one whose magnitude of response is directly proportional to the magnitude of the impressed disturbance—only frequencies present in the disturbance are represented in the response.

For a body whose magnitude of response is not directly proportional to the magnitude of the impressed disturbance—that is, for a non-linear body—the principle of superposition of forces does not hold. If several disturbances act simultaneously on a non-linear body, the resultant response contains product terms of the disturbance as well as summation terms, and frequencies appear in the response which are not present in the original disturbances.

A periodic body—that is, one whose impedance differs with the frequency of an impressed disturbance—may serve as a harmonic analyser, if its selectivity is sufficient. An electrical wave-metre whose circuit elements are all linear may be used to discriminate between the sinusoidal components of a complex disturbance. The presence of sinusoidal components in such wave-metre analysis, however, in no way proves the existence of such components in the original disturbance. In order to get a true representation of a complex disturbance the analysis must be made by a device whose response is both linear and aperiodic.

Modulation.

Modulation may be defined as a process which causes the multiplication of one periodic disturbance by another.

In the case of sinusoidal disturbances, for example, $A_1 \sin \omega_1 t$ and $A_2 \sin \omega_2 t$ modulate each other whenever the product $\sin \omega_1 t \sin \omega_2 t$ is obtained. From trigonometry

$$\sin \omega_1 t \sin \omega_2 t = 1/2 \cos (\omega_1 - \omega_2)t - 1/2 \cos (\omega_1 + \omega_2)t.$$

The product of the two terms is equivalent to two new disturbances having frequencies equal respectively to the sum and to the difference of the frequencies of the original periodic disturbances. These two derived frequencies are, if sound disturbances are used, the differ-

ential and the summation frequencies of Helmholtz. If a radio carrier wave is multiplied by audio frequency disturbances the derived frequencies are the sidebands.

EXPERIMENTAL STUDY.

Under the following headings experimental investigation of salient questions involved in the production and detection of combinational frequencies is described.

Does a resonant circuit respond when tuned to the difference in frequency between two separate oscillators ?

Two radio transmitters, one tuned to a frequency of 1,500,000 and the other to 526,315 cycles per second, were set up in the same room. A radio receiver tuned to a frequency of 973,685 cycles per second gave no response. When the receiver was tuned to either transmitting frequency loud response was obtained. When the two transmitters were tuned to nearly the same frequency beat notes were heard in the receiver. When one of the transmitters was tuned close to the frequency of a distant broadcasting station, beats between the carrier of the distant station and the local transmitter could be heard in the receiver. A third transmitter tuned to the difference in frequencies of the other two was then set up and all three operated simultaneously. No heterodyne whistles could be obtained in the receiver when it was tuned to the difference frequency.

If the medium through which radio waves are propagated is linear there is no condition giving modulation in the experiments described. The crystal receiver is a non-linear periodic circuit, but when it is tuned to one of the two transmitters and sufficiently detuned from the other to reject its frequency, only one wave impresses its voltage across the crystal. Only this signal is heard. When the two transmitters are tuned so nearly to the same frequency that the tuned receiver accepts both waves, then modulation by the non-linear crystal of the receiver produces sideband frequencies. These sideband frequencies are, in this case, manufactured in the non-linear receiving apparatus and do not exist in the linear medium which propagates the waves from the transmitters to the receiver.

The use of the terms "detection," "rectification," and "demodulation," with reference to the action of radio telephone receivers and of heterodyne continuous wave receivers, is misleading. The process actually involved is modulation. Modulation at a radio-telephone transmitter consists of multiplying a carrier frequency by audio frequencies to produce sidebands. Modulation at a radio-telephone receiver consists of multiplying one or both sets of sideband frequencies by the carrier frequency to produce new sidebands, one set of which is the band of audio frequencies used originally at the transmitter to modulate the carrier. The "first detector" of a superheterodyne receiver is really a non-linear element which causes product terms (modulation) of the signal frequencies and the locally generated frequency. This gives rise to sidebands, the lower set of which is the intermediate band used in the receiver.

Does a resonant circuit respond when tuned to a frequency equal to the difference between the carrier and the modulation frequency in the case of a modulated wave ?

Experiments made with modulated signals produced by Heising plate modulation circuits showed peak response in a linear wave-metre circuit at the sideband frequencies as well as at the carrier and modulation frequencies. The modulated wave is seen to be equivalent to three sinusoidal waves ; namely, the carrier and the two sidebands. These are distinguished by the peak response of the tuned wave-metre circuit which analyses the complex disturbance into sinusoidal components. The wave-metre circuit used in these experiments as the receiving device is a linear periodic circuit, and so introduces no modulation of its own. Circuits which have been published have employed detectors which left the response of a linear circuit to the sidebands a debatable question *. Fig. 1 shows a typical plot of current in the wave-metre circuit against the frequency to which it is tuned in the presence of a modulated wave. In the particular curve shown the carrier frequency was 36 kc. per second and the modulating frequency 10 kc. per second.

* For example, Colebrook's arrangement, 'Experimental Wireless and Wireless Engineer,' January 1931.

Under what conditions does the addition of two periodic disturbances produce summation and differential frequencies?

Two frequencies were added by coupling them to a common link circuit as shown in fig. 2. The link circuit contained only honeycomb coils, which are linear elements.

Fig. 1.

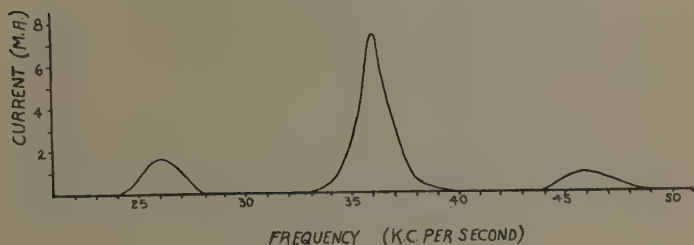


Fig. 2.

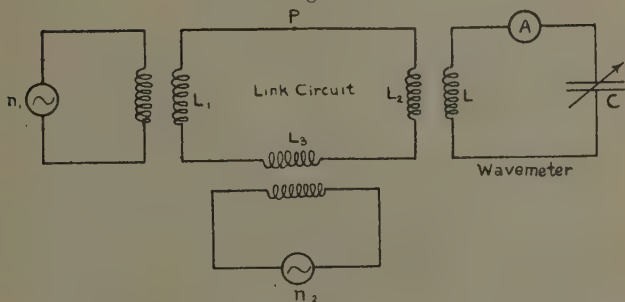
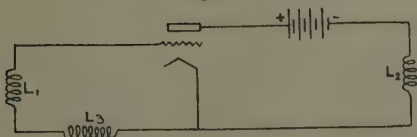


Fig. 3.



No deflexion in the wave-metre circuit was found when it was tuned either to the sum of frequencies n_1 and n_2 or to their difference.

A triode was then inserted at P in the link circuit, making the arrangement shown in fig. 3. When the

triode was operating on a curved portion of its grid voltage-plate current characteristic, peaks corresponding to $n_1 - n_2$ and $n_1 + n_2$ were obtained in the wave-metre circuit.

Similar response was obtained by using at P a diode formed by connecting the grid and plate of a 112-A tube together, as long as operation occurred on a curved portion of its plate potential-plate current characteristic.

These results show that combinational frequencies are produced by the addition of two periodic disturbances in a non-linear medium.

Electro-acoustical Wave-metre.

In order to make similar investigations in sound it was necessary to devise some form of acoustical wave-metre which would not involve use of the ear. Attempts made to pick out the components of complex sounds

Fig. 4.



by means of a set of Koenig resonators were altogether unsatisfactory. The mechanical manipulation of tuning by varying the length of resonators was crude and inconvenient, and the selection with certainty of the peaks present was altogether impossible with an untrained ear. Accordingly, an electro-acoustical wave-metre was constructed as follows :—

An iron core audio transformer was arranged with a primary which approximately matched the plate impedance of a 112-A tube and a secondary having an inductance of about 132 millihenries. The secondary was connected in series with a Weston thermo-milliammeter and a Leeds and Northrup decade condenser box having a range of capacities up to 1 microfarad. in steps of 0.001 microfarad. This circuit was tunable then over most of the audio band of frequencies. A carbon microphone was used as the sound pick-up device. The circuit is shown in fig. 4.

The sensitivity at 1000 cycles per second was such that one could produce full-scale deflexion of the milliammeter in the wave-metre circuit by whistling a 1000 cycle note with moderate intensity at a distance of four or five feet from the microphone.

This wave-metre was used in analysing sounds produced in various ways by loud speakers. When two speakers were placed close together and driven by separate oscillators, analysis showed the presence of only the two parent frequencies. When the wave-metre was tuned to either the sum or the difference frequencies no response was obtained, though full scale deflexion was obtained at either of the two combining frequencies. When the difference between the frequencies was small the milliammeter needle visibly wavered back and forth in unison with the beats, which were very loud.

Attempts were made to make two cone speakers modulate each other by coupling them together mechanically. Short pieces of aluminium wire were tried, and, failing in this, stretched rubber bands were used. No combinational tones could be detected by the wave-metre with any method of coupling used, though one could get full scale deflexions of the milliammeter at frequencies of either parent tone. One must conclude from these experiments that the addition of two sound waves in air does not produce appreciable differential or summation frequencies, though the ear responds easily to the beats. Neither does the coupling by mechanical connexion of the speakers cause the differential or summation tones to be emitted.

In the light of these experiments it is easy to understand why Koenig and Preyer did not find objective combinational tones. They experimented with tuning forks as separate sources. No product terms were involved, and simple addition of the sound disturbances in a linear medium produces no disturbance at the difference or at the summation frequency. While these experimenters used their ears in the detection of the resulting frequencies, they listened for re-enforcement in linear tuned bodies, such as forks and Koenig's resonators. They failed to observe such response because no combinational frequencies are produced under these conditions.

Bosanquet confirmed the results of Koenig and Preyer

because the precautions which he took to exclude external sound from both ears made it all the more certain that response in the resonator was the thing he would hear. He did not hear such response, because he had no condition giving modulation.

Edser and Rucker demonstrated how difficult it is to get acoustical modulation—that is, modulation of one sound wave by another. Even with their use of a double siren instead of separate forks as sources, the amplitude of the combinational tones was so small as to require the interferometer method of detecting response of a tuned resonator. The sensitivity of their detecting apparatus and the smallness of the response in no way casts doubts on the observations which Helmholtz and Lord Rayleigh made with their ears, for the human ear has the extremely low threshold of audibility of about 0.0004 dynes per square centimetre (r.m.s. value).

Is a non-linear element necessary to produce sidebands ?

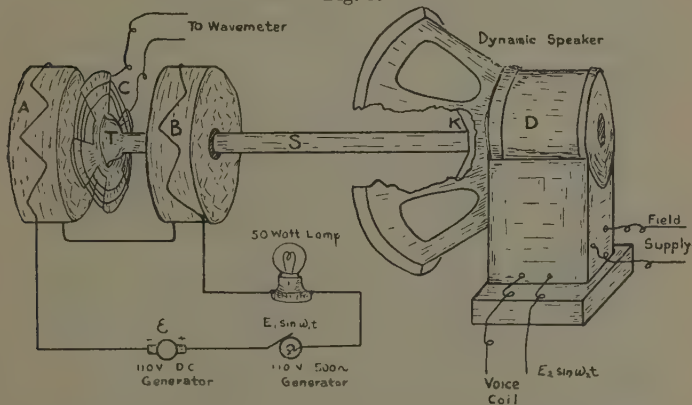
In the Heising method of plate modulation it seems that no non-linear element is employed. However, there may always be some doubt whenever a vacuum tube is used. Furthermore, many writers explain the production of sidebands by sending modulating current through the field windings of an A.C. generator as arising from the non-linear characteristic of the iron core. To test whether the sidebands can be produced without an iron core or any other possibility of non-linear behaviour, the following experiment was performed.

A magnetic field was produced by two 1000 turn air core honeycomb coils A and B connected in series opposition, as shown in fig. 5. Current from a 500 cycle generator was superimposed on direct current through these coils. The coils could be adjusted separately and then clamped in position. A glass thistle-tube T with stem S in a horizontal position was waxed on to a cone K of a dynamic speaker and driven by it. On the bell-shaped end of the thistle-tube there was waxed a 200 turn spider-web coil, which was connected to the wave-metre described in fig. 4 with the microphone omitted. This coil, C, which was very light, was driven back and forth parallel to the axis TS by the speaker. The coil then served as an armature of an air core generator, and cut the radial field produced by the two adjacent

faces of the honeycomb coils. The glass tube was made about 16 inches long so as to remove the coil C from any stray field of the speaker.

The field produced by the coils A and B is due to the direct current through the coils and to the superimposed instantaneous value of the current furnished by the A.C. generator. Each current has an axial component parallel to TS and a radial component from T in the plane of the coil C. In order to prevent the axial component of the variable field from inducing an e.m.f. in C, exact positions of coils A and B were chosen so as to balance out this effect. Practically this was done by tuning the wave-

Fig. 5.



metre to the frequency $\omega_1/2\pi$ with the coil C motionless and then varying the position A, B, and C until minimum deflexion resulted in the wave-metre. When this effect of the axial field is diminished to a negligible quantity, we need to consider only the radial field. The radial field may be represented by

$$\text{Radial field} = H_0 + H \sin \omega_1 t,$$

where ω_1 is the angular velocity of the A.C. generator. If the coil C is driven at a rate given by $A \sin \omega_2 t$, where ω_2 is the angular velocity of the current impressed on the voice coil of the speaker, then the e.m.f. induced in coil C due to its motion through the radial field is given by

$$e = kA[H_0 + H \sin \omega_1 t] \sin \omega_2 t,$$

where k is a constant. From trigonometrical relations this becomes

$$e = kA[H_0 \sin \omega_2 t + H/2 \cos (\omega_1 - \omega_2)t - H/2 \cos (\omega_1 + \omega_2)t],$$

which is an equation of the familiar carrier and sidebands form.

Experimental tests with the coil C vibrated at several different frequencies from 80 to 200 cycles per second, and with the frequency of the A.C. generator at 450 cycles per second, gave peak response in the wave-metre at the summation frequencies. Since the inertia of the glass tube connecting the speaker cone and the coil C limited vibrations of the coil to frequencies below 200 cycles per second, the wave-metre could not be tuned to the difference frequency. These tests show conclusively that modulation is produced by an arrangement causing a product of terms whether there is a non-linear element involved or not.

Summary.

1. There is a difference between beat tones and differential tones. Beat tones, produced by mere addition of frequencies, elicit no response in detecting devices tuned to their frequency.

2. Combinational tones or sidebands have objective existence if peak response in a linear periodic circuit is used as the criterion of existence. These derived frequencies are produced by modulation, which is the multiplication of one periodic disturbance by another.

3. Modulation can be secured either in linear or non-linear circuits.

4. Sound waves do not appreciably modulate one another in air, and their sources do not give appreciable modulation even when coupled together mechanically.

5. The Helmholtz-Koenig combinational tone controversy was due to misunderstanding of the conditions for modulation and failure of the experimenters to make their receiving devices independent of the ear.

6. The sideband controversy was based on vague definitions of physical existence and upon the illegitimate use of non-linear elements in detecting apparatus.

In conclusion, the writer wishes to acknowledge, with sincere thanks, the helpful guidance of Prof. R. R. Ramsey of Indiana University.

VIII. *On the Electrification of Dust Particles blown by an Air Blast.* By U. NAKAYA, D.Sc., Professor of Experimental Physics, and TÔITI TERADA, M.Sc., Physical Laboratory, Faculty of Science, Hokkaido Imperial University, Sapporo, Japan *.

[Plate IV.]

1. *Introduction.*

IT is well known that the dust particles of any substance are strongly electrified when they are blown by an air blast. Rudge † in 1913 first measured the electrical charge of dust particles for various substances, and he proposed to explain the origin of the electrical phenomena associated with a dust storm in a desert, a volcanic eruption, or a snowstorm in a polar district by this phenomenon. Since then the problem has attracted the attention of many physicists and similar experiments were carried out by Stäger ‡, Kähler §, Shaw || and many others. Recently the possibility of igniting the explosive mixture in a coal-mine by a spark due to this phenomenon was examined by Blacktin and Robinson ¶. The results obtained by these investigators conflict with each other, being sometimes even opposite in the sign of charge. The methods of measuring the charge used by the persons above mentioned are more or less the same in principle; they measure with an electrometer the total charge of a mass of dust particles by receiving them on a collector such as a metal box or a wire gauze. These methods as a group may be called “macroscopic,” for the charge of the individual dust particle is not considered as a part of the question in these cases.

In this paper the authors describe the “microscopic” method for measuring the charge of individual dust particle and some results obtained thereby. This microscopic method has already been used by Ladenburg **

* Communicated by the Authors.

† D. Rudge, *Phil. Mag.* xxv. p. 481 (1913).

‡ Stäger, *Ann. d. Phys.* lxxvi. p. 49 (1925); lxxvii. p. 225 (1925).

§ K. Kähler and C. Dorno, *Ann. d. Phys.* lxxvii. p. 71 (1925).

|| P. E. Shaw, *Proc. Roy. Soc. A*, cxxii. p. 49 (1929).

¶ S. C. Blacktin and H. Robinson, *Safety in Mines Research Board Paper no. 43* (1928), no. 71 (1931).

** R. Ladenburg, *Ann. d. Phys.* iv. p. 863 (1930); vi. p. 581 (1930); xiv. p. 510 (1932).

and his collaborators in the study of an electrical gas purification. By employing the same method as used in Millikan's oil drop experiment, they measured the mode of charging up of an initially uncharged particle of dust in an atmosphere ionized by a point discharge or α -rays. The initial charge of the particle separated by friction was made as small as possible in those cases. The object of the experiments herein described is to measure this charge of a particle separated by friction, after the manner of Ladenburg's experiment.

2. *A Deflexion Method under Microscope.*

In order to see whether the dust particles blown out of a jet are electrified before they come in contact with the metal collector, the authors adopted an electric deflexion method under microscope. As soon as the particles were blown out of the nozzle of the jet they were made to pass through a space between two electrode plates that were connected to the terminals of a transformer. The electric field applied was 60 cycles and 3000 V/cm., and the path of the particle was photographed with a microscope by the method of dark field illumination. A similar method has already been used by Wells and Gerke * for taking a microphotograph of the paths of smoke particles, when they used a very slow air current, and consequently the frequency of the applied field was of the order of five cycles. In the present case, however, the particles were caused to drift swiftly, so that it was very difficult to take photographs of their path. This difficulty was overcome by taking special precautions regarding the plate and developer on the one hand, and regarding the adjustment of the illuminating system in order to give a sharp focussing on the other hand. The plate used was Wellington's soft spectrum, and it gave the best result when developed with Rodinal solution for a considerably long time, say forty minutes. The fine adjustment of the illuminating system was accomplished by a mechanism shown in fig. 1 *a*. The electrode plates and the holder, together with the glass jet for blowing out the dust cloud, are shown in fig. 1 *b*.

Two photographs of the paths taken by lycopodium powder are reproduced in fig. 2 (*a*) and (*b*) (Pl. IV.) in which

* P. V. Wells and R. H. Gerke, J. Amer. Chem. Soc. xli. p. 312 (1919).

(a) shows the straightness of the path when no electric field was applied, and (b) represents the regular sine form of the path when an alternating field was applied. From these pictures one sees clearly that those particles are already strongly electrified when they leave the nozzle of the jet. Similar photographs were obtained also with coal dust. From the amplitude of the sine wave one can calculate the charge of the particle if the radius of the particle is known. Assuming the spherical form

Fig. 1 a.

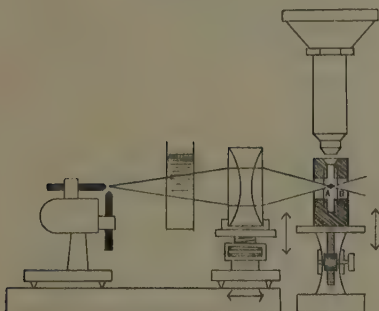
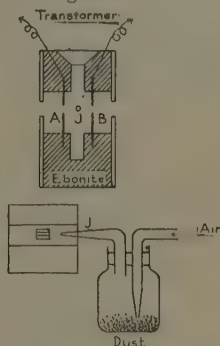


Fig. 1 b.



of the particle and a Stokes' resistance one gets the formula for the amplitude A ,

$$A = \frac{eY_0}{m\nu\sqrt{\nu^2 + \left(\frac{6\pi\eta a}{m}\right)^2}}$$

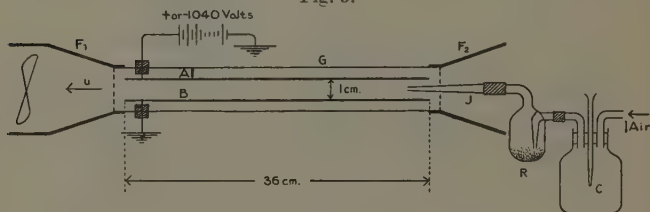
in which Y_0 is the amplitude of the applied field, ν is the frequency, and η , a , e , m are usual symbols. For the particle showing an amplitude of 1 mm., e becomes 1.3×10^{-7} e.s.u. if a is taken as 10^{-4} cm., and 1.4×10^{-6} e.s.u. if a is taken as 10^{-3} cm. These figures are in the same order of magnitude as the values obtained later by using a Millikan condenser.

3. Separation of the Positive and Negative Particles by an Electric Field.

By the method above described one cannot see the sign of the particle. In order to determine the sign the

authors tried to separate the positive and negative particles by a direct electric field. Relating to the problem of an electrical gas purification, Rohmann* used a similar method for measuring the e/m of dust particles. In the present case, however, difficulty arises from the fact that the velocity of ejection of the particles is considerably large, and also there are mixed many fine particles which are deflected with difficulty; accordingly it is necessary to let the dust cloud flow in the form of a slender pencil for a long distance, traversing the electric field. For this purpose the authors constructed a wind tunnel as shown in fig. 3. A and B were two electrode plates 36 cm. in length and 3 cm. in width, the distance between which was kept at 1 cm. These plates were inserted in a glass cylinder G, which was

Fig. 3.



provided with two metal funnels F_1 and F_2 . A fan was set in F_1 and it rotated slowly to raise a gentle breeze of velocity u through the cylinder. Adjusting the velocity u and also the pressure of the air producing the blast, it was possible to obtain a long narrow pencil of the cloud stream traversing the whole length of the electric field. The adjustment was made by using a stream of smoke. R was a light glass bottle with a very thin wall which was used for weighing the amount of dust that was blown out. C was a capillary tube for adjusting the pressure of the air.

With this arrangement it was possible, using an electric field of the strength 1040 V/cm., to separate the positive and negative particles very nicely. This was proved by using the mixture of red lead and resin powder, which is the usual mixture for making dust figures.

* H. Rohmann, *Zeits. f. Phys.* xvii. p. 253 (1923).

After having blown this mixture for a little while, the inside surfaces of the electrode plates were examined, and it was verified that the positive plate was covered with the yellowish white powder of resin and the negative plate was stained red with the red lead.

As a first series of the experiments, finely ground coal dust was kept in the bottle R, and the air draft was set going for a while. After stopping the air the inner side of the electrode plates, previously covered with white paper, was examined, and it was found that both plates were stained black colour in the same degree, showing that there were both positive and negative particles in almost the same amount. The blackness was most concentrated near the nozzle of the jet, and it

TABLE I.

	Initial amount of dust.	Amount of dust blown out.	Amount of neg. dust.	Amount of pos. dust.	The ratio —/+.	Mean.
Resin powder.	3.5374 gr.	1.5914 gr.	111.0 mgr.	96.5 mgr.	1.16	1.17
	3.6412 „	0.4481 „	21.8 „	20.6 „	1.06	
	6.0691 „	0.4921 „	49.5 „	43.5 „	1.14	
	5.5240 „	0.2805 „	38.0 „	28.5 „	1.33	
	5.5320 „	0.3451 „	57.5 „	49.8 „	1.15	
Coal dust.	5.7557 „	0.3091 „	55.1 „	39.7 „	1.39	1.70
	5.4466 „	0.5675 „	154.5 „	103.4 „	1.49	
	4.8791 „	0.4681 „	89.3 „	36.9 „	2.39	
	4.4110 „	0.6265 „	95.4 „	50.3 „	1.90	
	3.7845 „	0.7388 „	100.6 „	74.8 „	1.35	

faded out along the direction of the stream, the paper being almost white at the other end of the electrode plate. In order to determine the amounts of the positive and negative particles, the inner sides of the electrode plates were covered with thin cellophane paper, and the amount of dust attached to the paper was weighed by a chemical balance. The amount of dust blown out was also determined by weighing the reservoir together with the jet before and after turning on the air current. Two series of the experiments were carried out with coal dust and resin powder respectively. The results are tabulated in Table I. In order to avoid the effect due to the unsymmetry of the position of the jet with respect to the electrode plates, successive data were

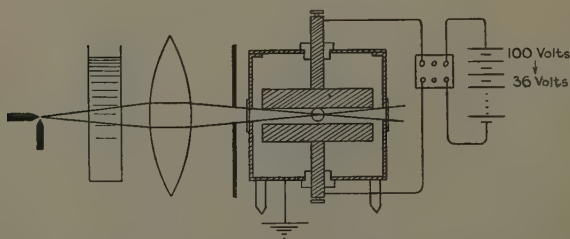
taken by changing alternately the sign of the applied voltage in the sequence of the measurements.

In the table one sees that the amount of the negative particles is always larger than that of the positive particles, this being more remarkable in the case of coal dust. If one receives these particles on a collector and measures the charge, the electrometer will show the difference of the charges of these positive and negative particles. As a matter of fact, the authors saw in a preliminary experiment that this coal dust gave a negative charge by a macroscopic method, which is concordant with the present result. The resin powder gives a small amount of charge when measured by a macroscopic method, which is also explained by the fact that the ratio of the negative particles to the positive is nearly unity. From this experiment one will be able to understand the meaning of the charge of dust particles measured by the usual macroscopic method.

4. *Measurement of the Charge of a Particle by the Millikan Condenser.*

In order to see the relation between the charge of the particle and its equivalent radius when one considers

Fig. 4.



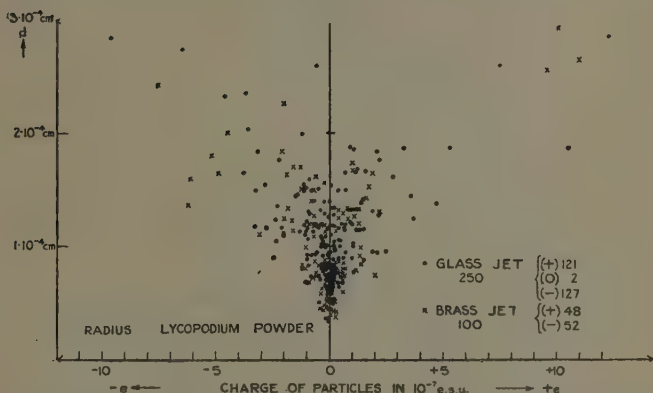
it as spherical, a similar experiment to Millikan's oil drop experiment was carried out. The condenser used for the purpose was made of thick copper plate and its sketch is shown in fig. 4. The distance between the plates was kept at 1 cm. throughout the experiments. The vessel was also made of copper plate and was provided with four windows—two in the sides for the purpose of illumination, one in the front for observation, and one

in the back wall for blowing the dust particles into the vessel. The observation was made by a reading microscope, and the velocity of free fall v_g and the upward velocity with a counter electric field v_e were measured. From these data one can calculate, after Millikan, the values of e and a by the equations

$$e = \frac{4\pi}{3} \left(\frac{9\eta}{2} \right)^{3/2} \left(\frac{1}{g\rho} \right) \frac{(v_g + v_e)}{X} v_g^{1/2}$$

$$a = \left(\frac{9\eta}{3g\rho} \right)^{1/2} v_g^{1/2}$$

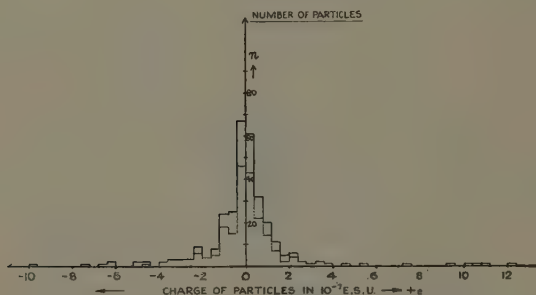
Fig. 5.



Two series of experiments were carried out with lycopodium powder and coal dust respectively. For lycopodium powder the e and a of 350 particles were measured, among which 250 particles were blown out by using a glass jet and 100 particles by an earthed brass jet. The values of e and a are plotted in the diagram shown in fig. 5. The \circ marks show the particles blown out of a glass jet and the \times marks those of an earthed brass jet. In the diagram one sees, although the points are scattered rather at random, these general tendencies:— (a) the particles of smaller charge are more abundantly observed than those of larger charge, (b) the larger particles are more electrified than the smaller ones, (c) the relation between the amount of charge and the

size of particle is more or less the same for the positive and the negative particles, (d) the numbers of the positive and the negative particles are nearly equal, (e) no marked difference is observed in the distribution of the points for both cases of a glass jet and an earthed brass jet. From the data in the diagram the authors constructed a frequency curve of the charge of the particles, which is shown in fig. 6. The dotted line gives the results for 250 particles blown through a glass jet and the full line for the total 350 particles. In both cases the frequency curve represents a form similar to a Gauss's probability curve. In the figure one sees clearly that most of the particles are slightly electrified and the

Fig. 6.



strongly charged particles are few in number. All these results will be explained by considering that the electricity of the particle is chiefly produced by the separation of charge due to a mutual friction between particles.

Similar experiments were carried out for coal dust with more or less similar results. For coal dust 120 particles were observed, among which the positive particles numbered 53 and the negative 67. Although the data are not sufficient for deducing any statistical conclusion, one sees that the negative particles exceed in number that of the positive, which is concordant with the experiment described in the preceding article. The charge of the coal dust was in general larger than that of the lycopodium powder, being nearly twice as large.

5. *Concluding Remarks.*

From the experiments described above the authors are led to the conclusion that the charge of dust particles is chiefly produced by a mutual friction between them, and consequently the particles blown out by an air blast are composed of positive and negative particles mixed together. It is already known that the electricity is separated by a mutual friction between the substances of apparently the same material. There are some theories on the cause of this phenomenon, such as the old theory which tries to explain it by the difference in curvature of the particle, or Shaw's theory *, which explains the difference in the electrical nature of the substances by their surface strains. Another possible cause may be some phenomenon such as a Lenard effect of solid substances, which is supposed by some people in their dynamical theories of a frictional charge.

There is, however, another important factor controlling this phenomenon; that is, the abundance of either the total positive or negative charge which is proper to the material of the dust in an algebraic sense. For example, in the case of coal dust the total charge measured macroscopically shows always a negative sign, excepting some rare occurrences of positive sign. The missing charge may be conveyed away by the air or by very fine particles which escape the mesh of the collector, or it may be conducted to earth through the wall of the reservoir. Rudge † attributes the missing charge to the air or very fine particles. In their microscopic observation by a Millikan condenser the authors could not measure the particles whose radii are less than 3×10^{-5} cm. It is possible that the ultramicroscopic particles below this limit may play some important rôle in controlling the abundance of the charge of one sign, but the present experiment does not show any evidence.

Experiments are now being continued by using the microscopic methods above described, in parallel with the usual macroscopic method, the results of which will be published in a future communication.

* P. E. Shaw and R. F. Hanstock, *Proc. Roy. Soc. A*, cxxviii. p. 474 (1930).

† D. Rudge, *Proc. Roy. Soc. A*, xc. pp. 256, 574 (1914).

IX. *Equations of Motion for a General System of Two Particles.* By W. H. WATSON, McGill University *.

§ 1.

IN the non-relativity dynamics of a system of two particles the connexion between the particles is set up by Newton's Third Law. On integration of the equations this leads to conservation of momentum for the system. When special relativity is taken into account, however, the Newtonian Third Law retains its meaning only so far as contact-action is concerned; in all other cases it is necessary to introduce some hypothesis as to the law of propagation of force from one point of space to another in order to remove the ambiguity which exists as to how the law is to be applied. If the particles have electrical properties the action and reaction of one on the other is taken account of through the laws of electrodynamics. According to the method due to Maxwell, which has up to the present almost completely dominated electrodynamics, the electromagnetic field is regarded as a physical existent and is treated as part of the dynamical system. Wherever there is a field there is energy and momentum localized in accordance with the well-known formulæ of the classical theory. On the quantum theory the classical formulæ yield the expectation of energy and momentum in place of the actual quantities themselves. This difference does not reside in the physical model but in the laws to which its behaviour is subject. It is this model which was used by Heisenberg and Pauli⁽¹⁾, to whose theory of the field serious objections have been pointed out by Dirac⁽²⁾.

So far as experiment goes we are ignorant of any actual field except where there are or have been objects by means of which to measure it. If these objects do not themselves show the mechanical effects of the field the electrical instruments on which they can act exhibit mechanical effects. It appears, therefore, that the idea of the electromagnetic field and the laws of electricity serve merely to calculate the dynamical interactions in the system of objects participating in an electrodynamical phenomenon. But this is not so as long as we retain the conservation of energy and momentum; it is *necessary*

* Communicated by the Author.

in Maxwell's theory to conceive of energy and momentum located in the space between and around the objects. A little reflexion shows that this is because in classical theory we require the conservation of energy and momentum reckoned instantaneously and continuously, and because we know as a fact that when one body loses energy another body does not immediately gain it. The field appears as a convenient invisible required to balance energy and momentum accounts. As soon as we give up requiring this balance we free ourselves from the need to treat the field as part of the dynamical system on the same basis as the particles. In an important sense the field components have the same logical status as the momentum components of the particle; the field need not be endowed with substantiality any more than any other vector field employed in mathematical physics.

Now the essence of the notion of a field acting on a particle is that it connects different orbits of the particle in it. It is therefore a property of a system of orbits. This point of view with regard to the electromagnetic field was advocated in a recent paper⁽³⁾ by the writer. Any given electromagnetic field can be regarded as a property of trajectories of an electrified particle in that field. It was shown that if $(P_x, P_y, P_z, iK/c)$ is the momentum 4-vector, and if the system of trajectories is properly chosen so that the components of the 4-vector are assigned suitable values at all x, y, z, t , then the Pfaffian form

$$\omega = P_x dx + P_y dy + P_z dz - K dt,$$

which represents the system of trajectories, implies the electromagnetic field components as the coefficients of the first derived form of ω multiplied by a factor depending on the units.

It is an obvious step to attempt to extend the method to the case of two (or more) particles, but it is difficult to make much progress unless we treat t on a different basis from the spatial coordinates, and then the equations of motion will no longer be covariant with respect to Lorentz transformations; consequently what follows is only a classical approximation. This device was used by Dirac in treating the motion of two particles in relativistic quantum-mechanics⁽⁴⁾, although the step does not receive notice in the calculation referred to.

$$\text{Now} \quad \frac{\partial T}{\partial \dot{x}} = mc^2 \frac{\partial \beta}{\partial \dot{x}} = \frac{\partial P}{\partial \dot{x}} \dot{x} + \frac{\partial Q}{\partial \dot{x}} \dot{y} + \frac{\partial R}{\partial \dot{x}} \dot{z},$$

$$\beta^2 = (1 - (\dot{x}^2 + \dot{y}^2 + \dot{z}^2)/c^2)^{-1},$$

and similarly

$$\frac{\partial T'}{\partial \dot{x}'} = \frac{\partial P'}{\partial \dot{x}'} \dot{x}' + \frac{\partial Q'}{\partial \dot{x}'} \dot{y}' + \frac{\partial R'}{\partial \dot{x}'} \dot{z}';$$

therefore

$$\begin{aligned} \frac{dP}{dt} &= \frac{\partial P}{\partial t} + \frac{\partial W}{\partial x} + \left(\frac{\partial P}{\partial y} - \frac{\partial Q}{\partial x} \right) \dot{y} + \left(\frac{\partial P}{\partial z} - \frac{\partial R}{\partial x} \right) \dot{z} \\ &\quad + \left(\frac{\partial P}{\partial \dot{x}'} - \frac{\partial P'}{\partial \dot{x}} \right) \dot{x}' + \left(\frac{\partial P}{\partial \dot{y}'} - \frac{\partial Q'}{\partial \dot{x}} \right) \dot{y}' + \left(\frac{\partial P}{\partial \dot{z}'} - \frac{\partial R'}{\partial \dot{x}} \right) \dot{z}', \\ \frac{dP'}{dt} &= \frac{\partial P'}{\partial t} + \frac{\partial W}{\partial x'} + \left(\frac{\partial P'}{\partial y'} - \frac{\partial Q'}{\partial x'} \right) \dot{y}' + \left(\frac{\partial P'}{\partial z'} - \frac{\partial R'}{\partial x'} \right) \dot{z}' \\ &\quad - \left(\frac{\partial P}{\partial \dot{x}'} - \frac{\partial P'}{\partial \dot{x}} \right) \dot{x} - \left(\frac{\partial Q}{\partial \dot{x}'} - \frac{\partial P'}{\partial \dot{y}} \right) \dot{y} - \left(\frac{\partial R}{\partial \dot{x}'} - \frac{\partial P'}{\partial \dot{z}} \right) \dot{z} \\ &\quad \dots \dots \dots (3) \end{aligned}$$

and four other equations.

In order to throw these equations into Lagrangian form it is necessary to introduce a vector-potential with six components $a_x, a_y, a_z, a_x', a_y', a_z'$, and a scalar potential ϕ , from which the forces are derived by a curling operation, according to equations of the type

$$\begin{aligned} x, t &= -\frac{1}{c} \frac{\partial a_x}{\partial t} - \frac{\partial \phi}{\partial x}, \quad x, y = \frac{1}{c} \left(\frac{\partial a_x}{\partial y} - \frac{\partial a_y}{\partial x} \right), \\ x', x &= \frac{1}{c} \left(\frac{\partial a_x'}{\partial x} - \frac{\partial a_x}{\partial x'} \right). \end{aligned}$$

The Lagrangian function is then

$$\begin{aligned} L &= mc^2(1 - \beta^{-1}) + m'c^2(1 - \beta'^{-1}) + \frac{1}{c} (a_x \dot{x} + a_y \dot{y} + a_z \dot{z} \\ &\quad + a_x' \dot{x}' + a_y' \dot{y}' + a_z' \dot{z}') - \phi, \end{aligned}$$

where m, m' are the respective masses of the particles. The Hamiltonian function is

$$H = c\sqrt{m^2c^2 + J^2} + c\sqrt{m'^2c^2 + J'^2} + \phi,$$

where

$$J^2 = P^2 + Q^2 + R^2, \quad \text{and} \quad P = p_x - a_x/c \text{ etc.}, \quad W = H - \phi. \quad \dots \dots (4)$$

The system of orbits from which we started is therefore obtained by assigning to each point x, y, z, x', y', z', t , the set of values P, Q, R, P', Q', R', W given by equations (4), where the p 's are derived from one solution of the Hamilton-Jacobi partial differential equation⁽⁵⁾.

Thus by proceeding in this way from the dynamical system represented by the Pfaffian form ω we have obtained a Lagrangian function which is formally the same as that for two charged particles in an electromagnetic field⁽⁶⁾. In order to take account of a given field and the electromagnetic interaction between the particles $a_x, a_y, a_z, a_x', a_y', a_z', \phi$ must be assigned the proper forms. But it is evident that the general system of two particles (without any restriction of the potentials) will not allow itself to be described in terms of the substance electricity in ordinary space and time. By considering the symbolic form adjoint to (2), and proceeding as in (I) §2, we can see that the 21-component field is to be treated in terms of the motion of a substance in the 6-space $xyzx'y'z'$. Under certain circumstances this degenerates into the motion of a substance in 3-space⁽⁷⁾. However, as the application of these ideas in the general case seems at present to be remote, there is no point in giving the detailed analysis here. From the logical point of view it is of importance that there is a method (indicated here) which gives the possibility of escaping systematically from the restrictions placed on our thoughts about nature by our regarding electromagnetic theory, whether in its classical form or its more modern copies, as the theory of the properties of a substance which "really exists" in the world. Rather is it a scheme of definite mathematical form, and of a certain comprehensiveness derived from its dynamical foundations, for describing what happens.

References.

- (1) *Zeits. für Physik*, lvi. p. 1; lix. p. 168 (1929).
- (2) Dirac, *Proc. Roy. Soc. A*, cxxxvi. p. 454 (1932):—"We cannot therefore suppose the field to be a dynamical system on the same footing as the particles, and thus something to be observed in the same way as the particles."
- (3) "Discontinuity in Electromagnetism." *Trans. Roy. Soc. Can.* xxviii. (1934), referred to as I.
- (4) Dirac, *loc. cit.* p. 461, equation (7).
- (5) I., p. 5.
- (6) Cf. Darwin, *Phil. Mag.* xxxix. p. 543 (1920).
- (7) For the decomposition of the integral invariant involved see Goursat, 'Problème de Pfaff,' p. 230.

X. *The Diffraction of β -rays. A Verification of de Broglie's Law for very High Velocity Electrons. By J. V. HUGHES, B.Sc., A.R.C.S., D.I.C.**

Introduction.

ACCORDING to de Broglie ⁽¹⁾, all particles in motion are accompanied by waves, the wave-length λ associated with a particle of mass m and velocity v being

$$\lambda = \frac{h}{mv}$$

where h is Planck's constant of action. Calculation shows that for slow electrons (for which the wave-length is greatest) the wave-length is of the same order as that of X-rays. Thus natural crystals should provide suitable diffraction gratings for electrons also, and under proper conditions a beam of electrons reflected from a crystal should give rise to a diffraction pattern.

This prediction has been verified for electrons up to 250 kv. energy. In the region of slow velocity electrons the first verification was by Davisson and Germer ⁽²⁾, who succeeded in showing that the wave-length varied inversely as the velocity of the electrons. They were not so successful with the absolute magnitude of the wave-lengths, which was first successfully checked in the medium velocity range by G. P. Thomson.

Davisson and Germer used a single crystal of nickel, and recorded the scattered electrons electrically. Subsequently Rupp ⁽³⁾ also verified the law in this region of electron velocities (energies 50–400 volts) using photographic recording, and observing the electrons transmitted through thin films of a number of materials, all polycrystalline and hence giving patterns of the well-known Hull-Debye-Scherrer type (rings concentric round the central spot).

Shortly after the first verification for slow velocity electrons by Davisson and Germer, G. P. Thomson ⁽⁴⁾ verified the law for electron energies of 5–50 kilovolts, using transmission and photographic recording. He was able to verify in this research not only the form of the

* Communicated by Prof. G. P. Thomson, M.A., F.R.S.

law, but also that the magnitude of the wave-length was that given by the law. The majority of the electron diffraction work has been carried out in this energy range, and the law incidentally been verified by a large number of workers. This range now reaches to about 150 kv.

The highest energy for which the law has so far been verified is 250 kv., achieved by Rupp ⁽⁵⁾. He also utilized the method of transmission by a polycrystalline film, and photographic recording.

Kosman and Alichanian ⁽⁶⁾ have succeeded by this method in diffracting electrons of 520 kv. energy. However, they assumed the law under discussion, and deduced the energy of the electrons used (which they could not measure otherwise) from the diameters of the rings obtained.

The accuracy claimed for most of these determinations is about 1 per cent. Rather less accuracy is attained for the low and for the high velocity ranges, and slightly more for the intermediate (5-100 kv.) range.

In the experiment here described it was decided to attempt to diffract the β -rays from a radioactive source. In this way electrons of extremely high energy (250-1000 kv.) were available, and so the range within which the law has been verified could be very considerably extended. In addition, it adds one more item of evidence for the identity of β -rays and electrons.

There is one point to note: in the above formula for the wave-length, m is the actual mass of the body when in motion. If m_0 be the mass of the body when at rest and $\beta = \frac{v}{C}$ where C is the velocity of light, then the formula can be written

$$\lambda = \frac{h\sqrt{1-\beta^2}}{m_0v}.$$

This is of importance when the theoretical wave-length is deduced from a voltage measurement. In the case of the β -rays, however, the quantity which is always measured is their " $H\rho$ " value, where ρ is the radius of curvature of the path they would follow in a magnetic field of strength H . This is directly proportional to the momentum of the β -particle in flight, *i. e.* to mv , so that in this case the relativity correction causes no trouble.

The results obtained verify de Broglie's law, for electrons from 250 to 1000 kv. energy, to an accuracy of about 5 per cent.

Method.

The chief trouble to be dealt with is one of intensity. Whilst a current of 1 milliamp. can be obtained in a discharge-tube easily, the β -ray current from 1 millicurie of radon in equilibrium with its products is only of the order of 10^{-11} amp. This, moreover, comprises all velocities, so that if a particular velocity be sorted out the available current is much less. Clearly some sort of focussing must be used, and this must also sort out a single velocity (or monochromatic beam, as it is sometimes termed).

In selecting an appropriate focussing method the following points had to be borne in mind :—

(i.) Owing to the high momentum (small wave-length) of the β -rays the angle of diffraction would be small, so that as long a camera length as possible was required.

(ii.) It is preferable to have no fields inside the camera.

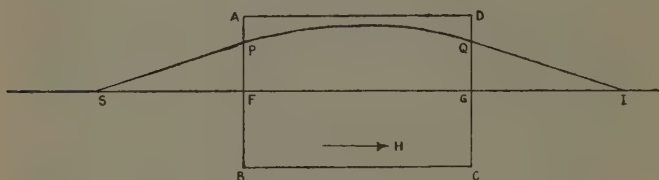
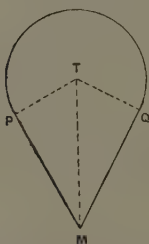
(iii.) Since the diffracting foil will have to be very thin, and hence delicate, as little of it as possible should be required.

(i.) and (ii.) render the usual semicircular focussing method for β -rays ⁽⁷⁾ inadvisable. Tricker ⁽⁸⁾ used a helical focussing device, but this transgressed (ii.) and (iii.).

Lebedeff ⁽⁹⁾ gave a method of using a focussing coil previous to the specimen, and a modification of this method was finally used. In his method a coil was used with its axis along the beam, and as shown by Busch ⁽¹⁰⁾ such a coil acts on electrons as a lens. However, unless such a coil be placed symmetrically between the source and the image, theory demands that it be thin. Calculation showed that a thin coil with the requisite number of turns could not be made. The action of such a coil depends mainly on the end effects of the coil. It was decided to use here a long coil, with axis along the direction of travel of the beam, and placed symmetrically between the source and the image. In this case the uniform portion of the field is of more importance than the end

effects, and the momentum of the focussed rays is proportional to the field in the coil. Since, as far as I am aware, this type of focussing (a long coil which, however, does not reach entirely from source to image) has not previously been described, a short outline of the action of this coil is given.

In fig. 1 *a* ABCD represents the coil, the direction of whose field, H , is indicated. S represents the source, I the image, and $SPQI$ the trajectory of some typical ray. In fig. 1 *b* a view along the axis is given.

Fig. 1 *a*.Fig. 1 *b*.

M stands for S, F, G, I .

From S to P the electrons travel in straight lines, diverging from S (field free space). From P to Q the electrons follow portions of helices round the lines of force. From Q to I the electrons once more travel in straight lines (field free space).

If the velocity of the electrons be such that they have just traversed the field by the time that they have been turned through such an angle as to be directed towards the axis, then they will pass through the axis, at I . Electrons of greater velocity will occupy less time in passing through the field, and hence will turn through a smaller angle (since the angular velocity of the electrons

in the field is independent of their velocity) and consequently will not again pass through the axis.

It is noteworthy in passing that the arrangement here described does not act as a lens whose focal length depends on the velocity of the electrons, in that it does not bring electrons of different velocities to foci situated at different points along the axis; rather it brings the electrons of the correct velocity to the focus, symmetrical with the source round the mean plane of the coil, and all other velocities have at best a circle of least diameter through which they pass.

To prove that all electrons of the correct velocity pass through the axis at the same point.

In fig. 1 *a* let $\hat{P}\hat{S}F = \theta$. Then we require to show that the position of I is independent of θ .

Let m be the mass (travelling mass when relativity effect is important)

v , the velocity;

e , the charge in e.m.u. of the electron;

H , the field strength;

ω , the angular velocity;

r , the radius of the circle (=PT or TQ in fig. 1 *b*),
followed by electrons in the field.

$$SF = x : FG = 2l.$$

Then $v \cos \theta$, $v \sin \theta$ are axial and radial velocities of electron, respectively, and $PF = x \tan \theta$.

We know $\omega = H \frac{e}{m}$, independent of both θ and v .

Angle turned through in field $= \frac{2l}{v \cos \theta} \cdot H \frac{e}{m}$, which is independent of θ as long as $\cos \theta$ can be taken as unity.

$$\text{In fig. 1 } b \quad PT = r = \frac{v \sin \theta}{H \frac{e}{m}}.$$

$$\text{Thus} \quad \tan \hat{P}\hat{T}\hat{M} = \frac{x}{v \cos \theta} H \frac{e}{m}.$$

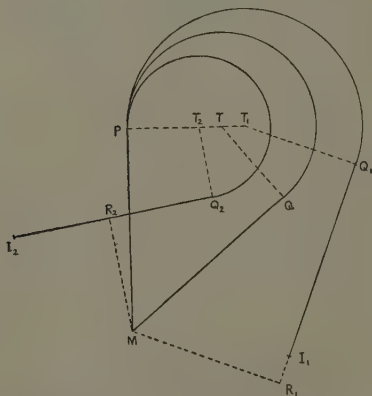
So that this angle is independent of θ to the same order of accuracy.

Thus, \hat{MTP} and the reflex angle PTQ (the angle turned through in the field) are independent of θ ; Q is the point where the electron leaves the field. Hence the direction of TQ is independent of θ .

It can be seen from fig. 1 *b* that the condition for focussing is that $Q\hat{T}M = \hat{MTP}$. If this is so for any value of θ it follows from above that it must be so for all values of θ for which $\cos \theta$ can be equated to unity.

In other words, if for one position of P a ray from S (of the correct velocity) passes subsequently through the axis, then rays from S for any position of P will do so.

Fig. 2.



It only remains to note that for any value of θ , $QM = PM$ and the axial and total velocities are unchanged by a longitudinal magnetic field, to see that all the rays must pass through the axis at some point I where $GI = FS$.

In fig. 2 are given the cases (viewed along the axis) for rays of greater (MPQ_1I_1) and of smaller (MPQ_2I_2) velocity than the focussed ray. From above we see that

(a) The angle $P\hat{T}M$ is smaller than the larger v (which means $P\hat{M}T$ larger the larger v) and is independent of θ .

(b) The angle $P\hat{T}Q$ is smaller the larger v , and is independent of θ .

(c) $I_1\hat{T}_1Q_1$ must be the same as $P\hat{T}_1M$ and similarly $I_2\hat{T}_2Q_2$ as $P\hat{T}_2M$, if I_1 and I_2 are points on the plane normal to the axis through I , the point of focus of the focussed rays.

(d) Thus the angles $M\hat{T}_1I_1$ and $M\hat{T}_2I_2$ are independent of θ : and since MT_1 and MT_2 are proportional to θ (strictly to $\tan \theta$) we see that MI_1 and MI_2 are proportional to θ ; or these rays cover all the zone up to the circle set by the extreme ray.

(e) Clearly the nearest to focus that the fastest rays will get will be a "circle of least radius," radius MR_1 , beyond the plane of I : and similarly the slower rays pass through a circle of least radius, radius MR_2 , before reaching this plane.

The above discussion also serves to give the value of the field required for any particular velocity. It is only necessary to notice that the condition for focussing is that

$$M\hat{T}Q = M\hat{T}P.$$

$$\text{But} \quad M\hat{T}P + P\hat{T}Q + Q\hat{T}M = 2\pi.$$

$$\text{Thus} \quad P\hat{T}Q = 2(\pi - M\hat{T}P).$$

Substituting the values already obtained for these angles

$$\frac{2l}{v \cos \theta} H \frac{e}{m} = 2 \left(\pi - \tan^{-1} \frac{x}{v \cos \theta} H \frac{e}{m} \right).$$

Assuming $\cos \theta$ to be taken as unity, and writing $\alpha = \frac{He}{mv}$ this reduces to

$$l\alpha = \pi - \tan^{-1} x\alpha$$

or

$$x\alpha = \tan(\pi - l\alpha),$$

an equation for α , which can be solved numerically. It will be seen that α is a constant, depending only on the geometry of the apparatus.

Hence from the definition of α , it follows that $H \propto mv$.

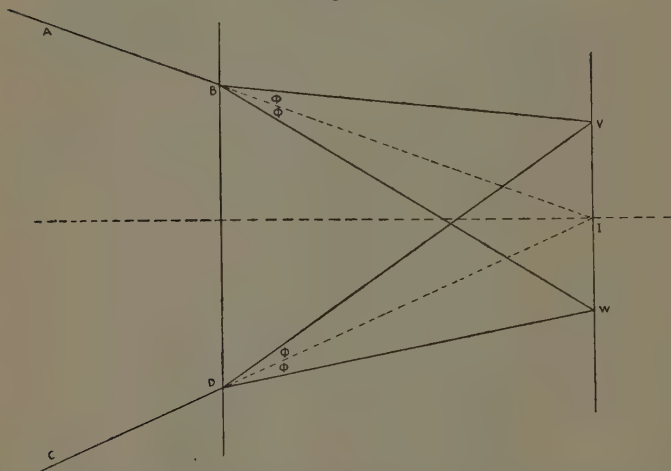
It will be seen that by this method of focussing a monochromatic beam is focussed, other rays being spread over the plate and merely forming a background. This, unfortunately, cannot be helped, and care must be taken to focus on one of the lines of the β -ray spectrum, so that

the background of unfocussed rays is relatively less intense; it nevertheless was a cause of considerable trouble, rendering the negatives very dense.

The diffracting foil is placed across the whole beam at some point in the field free space GI. The explanation of the formation of rings focussed in this way was given by Lebedeff ⁽⁹⁾. As this is the basis of the whole experiment it may be as well to recount it here.

Let ABI, CDI in fig. 3 represent two typical rays of a beam of electrons converging on I. Let BD represent

Fig. 3.



the diffracting foil, and VIW be a plane through I normal to the axis of the beam.

At B the ray ABI will suffer diffraction, and from B a cone of semi-vertical angle ϕ and axis BI will spread out (assuming we are dealing with a polycrystalline film), where ϕ is, of course, twice the Bragg angle of reflexion. The plane VIW will cut this cone in an ellipse, whose eccentricity for paraxial rays will, however, be very small: I is one focus of the ellipse.

All rays will give ellipses of this kind, with eccentricities varying between zero (circles, from the axial rays) up to the value for the extreme ray, and with the major

axes in the directions of the lines joining the axis to the points where the rays concerned pass through the foil. Thus for the whole foil the net result will be a ring whose inner and outer edges correspond to the perihelion and aphelion of the extreme ellipse. With paraxial rays such as we are limited to this breadth of ring is quite negligible, and the ring can be regarded as focussed: the mean diameter of the ring satisfies Bragg's law.

It will be seen that for a reasonable camera length and wide angle beam (within the paraxial limit imposed by the focussing theory) quite a large diameter diffracting foil is demanded. Owing to the focussing action parts of the diffracting foil may be blanked out without damage to the diffraction pattern, so that, as pointed out by Lebedeff, a gauze can be used to support the foil. Even with this help, however, the production of such large foils of the requisite thickness was the greatest difficulty in the execution of the experiment.

To prevent γ -rays from reaching and fogging the photographic plate, it was sufficient to have a cylinder of lead along the axis in the magnetic field in such a position that no rays travelling from the source in straight lines could reach the plate.

This also prevented axial rays of the wrong velocities (and, quite incidentally, of the required velocity too) from reaching the plate. Only rays which had actually suffered deviation by the magnetic field were able to reach the plate.

To conclude the theory the method of reducing the results might be given.

With the same notation as before (noting that " $H\rho$ " is a single quantity defining the β -ray):—

$$\text{We know} \quad H\rho = \frac{mv}{e}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{de Broglie's law} \quad \lambda = \frac{h}{mv}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\text{Bragg's Law} \quad \phi d = \lambda, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

for first order reflexion for planes separated d . But

$d = \frac{a}{\sqrt{n}}$ where a is the side of unit cube and n is the

sum of the squares of the Miller indices of the plane

involved; and $\phi = \frac{D}{2L}$ where D is the diameter of the ring for a camera length L .

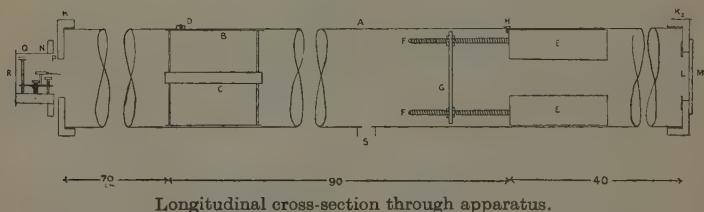
It follows that

$$\frac{D}{\sqrt{n}} \cdot H\rho \cdot \frac{1}{L} = \frac{2h}{ea},$$

a constant.

Hence for a given plate we first evaluate the mean $\frac{D}{\sqrt{n}}$ for the lines on it, and the product of this with the $H\rho$ value of the focussed beam should be a constant. Since on one occasion between two sets of results the camera length was changed, L is included in the Left Hand or variable side of the above equation.

Fig. 4.



From this constant the value of "a" can be deduced, and compared with its known value. Thus the constancy of $\frac{D}{\sqrt{n}} \cdot H\rho$ verifies the form of de Broglie's law,

and the evaluation of "a" checks the absolute magnitude of the wave-length which it forecasts.

Apparatus.

The apparatus consisted essentially of a single cold-drawn brass tube (A, fig. 4), 10 cm. diameter and 200 cm. long. Another brass tube B, 10 cm. long, which was a good sliding fit in A, carried by three rods at each end the lead cylinder C for stopping the γ -rays, as mentioned previously. This assembly was fixed in A by means of a grub screw working in the boss D soldered to the side of the main tube; the pointed end of this

grub screw engaged a V-groove cut round B. When in position the screw-head and boss D were waxed over.

A lead block E, 10 cm. long, was cast so as to slide easily in A. A hole 4 cm. in diameter through the centre allowed for the passage of the rays. The foil carrier G could be clamped by nuts on the three screwed rods F which projected from the end of E. This whole assembly for supporting the diffracting foil could slide in and out of A: its motion inwards was checked by the projecting end of a screw H, screwed through the wall of the main tube 40 cm. from the top, and soldered in position.

The ends of the tube A were fitted with cast brass end caps K_1 , K_2 , which screwed on strengthening brass rings soldered on the ends of A. In final assembly these caps were screwed on with yellow wax melted between the threads.

The upper cap had cut in it a rectangular hole L to take the photographic plate. No arrangement was made for moving the plate in or out of the beam, for since exposures of the order of days were anticipated, the time during which the vacuum was being obtained was not sufficient to cause the plate to be affected by scattered rays. This hole could be covered by a brass plate M waxed in position.

The source was mounted in a small brass stand, which could be mounted in a carrier capable of giving five adjustments of position. For the principle of this carrier I am indebted to Prof. Pollard. This was contained in a short brass tube Q, 5 cm. diameter by 4 cm. long, soldered to a thick brass plate N which, with the lower end cap, formed a flat ground joint P. The other end of the tube Q was sealed by a flat brass plate R soldered in position.

The lead stop C was centred in its tube B on the bench before being inserted in A. The source holder was clamped in position and the source carrier centred (from the back) against C after the latter's insertion a short distance into A. A centring template for this position was constructed; and only after this had been completed was the plate R soldered on to close the end of Q. Then the system BC was pushed to its final position and fixed, as explained above, and the end caps waxed on.

The focussing coil was 60 cm. long and wound on a 12 cm. diameter brass tube, and had 100 turns per cm. No cooling system was necessary. It was held in position by resting on a metal ring clamped round A, and centred by wooden rings at the top and bottom.

The whole apparatus was mounted approximately in the earth's magnetic field, being supported on two wooden stands carrying clamps round A. It was evacuated through the single port S, by wide-bore tubing, by a two stage Gaede mercury diffusion pump backed by a rotary oil pump.

Experimental.

The apparatus was first tested out and calibrated with cathode rays. To do this a discharge-tube mounted on a brass holder which carried the anode was used. This brass holder had a ground flat top which formed a ground joint with the lower end cap K_1 . The brass holder also carried side tubes for pumping and for a leak to regulate the pressure in the discharge-tube. A willemite screen on a cleaned photographic plate was placed in the hole L instead of the plate, and a thick glass slab waxed over instead of the plate M. With the discharge running, the current through the solenoid was adjusted until the spot on the screen was at the position of best focus, and the current noted. The potential difference across the discharge-tube was measured with a spark-gap. These readings were taken to the limit of the H.T. set available (80 kv.). For each voltage the corresponding $H\rho$ value for the electrons was calculated (using relativity formulæ) and the $H\rho$ value plotted against the current required to focus. Quite a good straight line resulted, which was extrapolated to give the approximate currents required for the more prominent lines of the Ra (B+C) spectrum of β -rays. This extrapolation was checked by noting the sharpness of focus of the spot for these currents when a Ra (B+C) source was used.

Despite the centre lead stop, the intensity of the focussed spot was sufficient to burn the willemite screen quite heavily.

After the above calibration a radon tube (radon contained in an α -ray tube to minimize the reduction in β -ray velocity by the glass walls) was put in the source holder, centred, and mounted by means of the flat ground

joint P (fig. 4) in place of the above-mentioned discharge-tube and brass holder. It was found impossible to see anything on the willemite screen (which, of course, was natural, as the calculated β -ray current in the focussed spot is only of the order of 10^{-16} amp.), so a photographic plate and the metal plate M were put in position. Firstly it was verified, as mentioned above, that a sharply focussed spot was obtained with the appropriate current in the focussing coil, and that deviations from these currents detracted from the sharpness of focussing. Then a number of foils were tried to obtain diffraction patterns. To change a foil it was only necessary to melt the wax fixing the top end piece K_2 , unscrew this and withdraw the lead block E and foil attachments complete.

Commercial gold foil was first tried, but was found to be unsatisfactory. Then commercial platinum foil was tried, first as produced, and subsequently in a built-up foil (on a wire frame) of the thinnest pieces selected from a number of leaves. Zinc oxide deposited on gauze from burning zinc was also tried, but none of these proved successful.

The magnitude of the task may be gathered when it is realized that a foil of the order of 10^{-5} — 10^{-6} cm. in thickness, of a diameter of about 5 cm., was required.

Recourse was had to sputtering, the usual method of sputtering on cellulose acetate, dissolving off the backing in acetone, and picking up the film from the liquid being adopted. It was found, however, to be impossible to get anything like the desired area of foil by this method, even in pieces. It should be pointed out that it was not sufficient to have only parts of the foil thin enough to diffract, for the thicker parts scattered the electrons, increasing the diffused background which was already serious owing to the action of the unfocussed rays.

Finally, Mr. R. Beeching drew my attention to the use of gelatine as a base for sputtering. In this process a gelatine solution just thick enough to "set" when cold was used. A fine mesh gauze was dipped in the warm solution, and with a little manipulation a good gelatine film of sufficient area could be obtained. Gold was then sputtered on to this, and the film used in this state. The gelatine was thin enough not to interfere with the electrons.

The sputtering was done from a horizontal gold wire carried on a ground joint with axis vertical. It was turned round the joint at timed intervals during the sputtering, so that a uniform deposit over the whole area of the gelatine was obtained. Success was finally obtained with films of this sort. Usually before sputtering on to a gelatine film the latter was used in the apparatus, to verify that it allowed the centre spot through and did not give rise to an appreciable scattered background (distinguished from the background of unfocussed rays by the fact that a scattered background would be denser nearer the centre spot). A number of films had to be used, as they were frequently damaged either in sputtering or evacuating and did not cover sufficient area, even when the correct film thickness had been found.

Results.

The majority of plates were tested on the line $H\rho$ 1938 (energy 264 kv). The strongest ring was the $\sqrt{3}$, $\sqrt{4}$, sometimes resolved and sometimes not (the ease with which the ring could be seen was in general the factor deciding whether the eye could separate it into two components or not; presumably it was always resolved instrumentally). The next occurring ring was the $\sqrt{11}$, $\sqrt{12}$ (certainly not resolved), and on one plate a very faint and broad ring was ascribed to the $\sqrt{19}$, $\sqrt{20}$. The numerical value taken for the $\sqrt{3}$, $\sqrt{4}$ unresolved was 1.84, this being a mean weighted in the ratio of occurrence of (111) planes to (200) planes. For the other unresolved lines an unweighted mean was taken.

Plates were also obtained for the lines $H\rho$ 2980 (energy 520 kv.) and $H\rho$ 4866 (energy 1037 kv.). On these plates usually the $\sqrt{3}$, $\sqrt{4}$ were the only visible rings, sometimes resolvable and sometimes not. On one plate the $\sqrt{11}$, $\sqrt{12}$ was sufficiently definite to be measured. On all these plates the background was so dense that they could only be viewed by holding them up to a 75 watt pearl bulb. This great density, along with the faintness of the rings, made it practically impossible to obtain a print suitable for reproduction.

The measurements of the ring diameters were made with spring action dividers, the mean of three measurements being taken.

First Set.

Plate no.	Details.	Current amp.	$H\rho$.	D cm.	\sqrt{n} .	$\frac{D}{\sqrt{n}}$.	Mean $\frac{D}{\sqrt{n}}$.	$\frac{H\rho}{D \sqrt{n}}$.
23 ...	6 hrs. at 40 millicuries.	0.73	1938	0.90	$\sqrt{3}$	0.520	0.505	978
				0.99	$\sqrt{4}$	0.495		
				1.62	$\sqrt{11, 12}$	0.478		
				2.32	$\sqrt{19, 20}$	0.525		
25 ...	1 day at 40 mc.	1.83	4866	0.32	$\sqrt{3, 4}$	0.174	0.174	847
26 ...	1 day at 40 mc.	1.83	4866	0.32	$\sqrt{3, 4}$	0.174	0.174	847
29 ...	1 day at 40 mc.	0.73	1938	0.91	$\sqrt{3}$	0.526	0.511	990
				0.99	$\sqrt{4}$	0.495		

Camera length 46 cm. Mean $H\rho \frac{D}{\sqrt{n}} = 916$.

Second Set : Plates 96, 99, 100 were the best obtained ; 97 and 98 were not as good.

Plate no.	Details.	Current amp.	$H\rho$.	D cm.	\sqrt{n} .	$\frac{D}{\sqrt{n}}$.	Mean $\frac{D}{\sqrt{n}}$.	$\frac{H\rho}{D \sqrt{n}}$.
96 ...	4 days at 40 mc.	0.73	1938	0.95	$\sqrt{3, 4}$	0.516	0.519	1005
				1.77	$\sqrt{11, 12}$	0.522		
99 ...	6 days at 60 mc.	1.83	4866	0.38	$\sqrt{3, 4}$	0.207	0.207	1006
100 ...	2 days at 100 mc.	1.125	2980	0.58	$\sqrt{3}$	0.335	0.338	1007
				0.65	$\sqrt{4}$	0.325		
				1.20	$\sqrt{11, 12}$	0.354		
97 ...	1 day at 100 mc.	0.73	1938	0.99	$\sqrt{3, 4}$	0.538	0.538	1043
98 ...	1 day at 100 mc.	0.73	1938	0.94	$\sqrt{3, 4}$	0.511	0.511	990

Camera length 48.4 cm. Mean $H\rho \frac{D}{\sqrt{n}} = 1010$.

Hence $H\rho \frac{D}{\sqrt{n}} \cdot \frac{1}{L}$ from 1st set = 19.9,
 from 2nd set = 20.9.

Taking $h = 6.55 \times 10^{-27}$ erg-sec. : $e = 1.59 \times 10^{-20}$ e.m.u.,

“ a ” from first set = 4.14×10^{-8} cm.

from second set = 3.94×10^{-8} cm.

Mean..... 4.04×10^{-8} cm.

The extreme closeness of this final mean to the accepted value of 4.06×10^{-8} cm. (as gold was the material) is, of course, fortuitous ; but the accuracy can be seen to be about 5 per cent. throughout ; the second set consists of much more clearly defined and more easily measurable plates, and so is more trustworthy, and it will be noted the agreement is much better in this set.

The energies to which these correspond are :

$H\rho$ 1938, 264 kv.,

$H\rho$ 2980, 520 kv.,

$H\rho$ 4866, 1,037 kv.,

so that de Broglie's law is verified up to energies of 10^6 volts.

One further point is worthy of mention. All the plates showed a series of white lines radiating from the centre. They were explained as being shadows of the rods supporting the centre lead stop C, thrown by unfocussed rays. Of course only prominent peaks on the β -ray spectrum were strong enough to throw these shadows when unfocussed, so that the shadows are discrete (instead of continuous corresponding to the continuous spectrum of β -rays). It has been suggested that this might have applications to analysis of β -ray spectra, as the resolving power could be quite high compared with the usual method.

Conclusion.

In the experiment described de Broglie's law has been verified, to an accuracy of 5 per cent., for electrons with energies ranging from 250 to 1000 kv. Thus de Broglie's law has now been verified for electrons over the whole range from 50 volts to 10^6 volts. These high velocity electrons were β -rays, a monochromatic beam being

selected by a magnetic field of original design which at the same time focussed a beam of considerable angle. Even then exposures of the order of days were necessary, with sources of 50 to 100 millicuries of radon. The diffracting foils used were sputtered gold on gelatine.

I must thank Prof. G. P. Thomson for suggesting the experiment and for much valuable encouragement and advice during its execution. I must also thank the Radium Committee of the Medical Research Council for the supplies of radon, without which the research would have been impossible, and Prof. Russ for advice on the handling of the radon. Also my thanks go to Mr. Spicer, of the Middlesex Hospital, who kindly prepared the sources for me, and to Mr. Crowe, who supplied me with the α -ray tubes used.

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XI. *The Mean Effective Pressure in Reciprocating Engines as influenced by considerations of the Kinetic Theory of Gases.* By H. H. JEFFCOTT, *Sc.D.* *

1. *Introduction.*

WHEN an engine piston is moving rapidly the pressure it experiences is influenced by the fact that the velocities of the molecules of the working substance, whether steam or gas, are not all much greater than the piston speed. According to the kinetic theory of gases the distribution of the velocity components in any direction when the gas is in a steady state is such that many of the

* Communicated by the Author.

molecules are momentarily travelling at relatively low speeds, many at relatively moderate speeds, and a smaller number at exceedingly high relative speeds. As a result the theoretical conclusion is reached that at high piston speeds there may be a diminution of transfer of momentum on impact of the molecules on the piston face, or of the gas pressure on the piston, of appreciable amount depending on the relative velocities of the piston and of the gas molecules. Now in the indicator, as ordinarily employed to record the effective pressure of the working substance, the velocity of the plunger is considerably less than that of the piston, and it thus appears that the effective pressure on the piston face may be less than that recorded on the indicator diagram. The object of the present paper is to present an approximate theoretical examination of this matter, and to suggest its experimental investigation.

2. We shall develop these considerations in more detail, and to fix the ideas shall have in mind a reciprocating engine.

For the purpose of the present investigation the working substance is presumed to be approximately in a steady state at the moment considered. In particular we will consider the time when the working substance is at the commencement of the expansion stroke. According to the kinetic theory of gases the substance consists of a very large number of molecules which at any instant are moving at different velocities throughout the space occupied. The impingement and recoil of the molecules from the cylinder walls give rise to the pressure to which they are subjected. While some of the molecules travel comparatively slowly, and others travel at very high velocities, the mean velocity of the molecules is high, but not extremely high, compared with the piston speed in high-speed engines.

We now conceive the condition of things in which the piston is moving rapidly forward in the cylinder under the action of the gas or vapour pressure. The pressure on the piston face is no longer that to which it was subjected while it was presumed to be at rest, for two reasons—firstly, by reason of the velocity of the piston the pressure caused by the impact of any chosen molecule is less than that in the static case, and, secondly, the time interval between the impacts of

molecules of any chosen value of velocity component is greater than if at rest, and those molecules whose components of velocity are less than that of the piston do not impinge upon it during the brief time interval considered.

3. We will first consider the simple case of a single elastic molecule impinging perpendicularly on the piston face.

Let the velocity of the piston before impact be represented by w ; then after impact its velocity will also be sensibly w . Let the velocity of the particle before impact be u , and after impact u' , the velocities u and u' being reckoned positive when in the same direction as w . Since the collision is elastic we have $u - w = w - u'$.

If the mass of the molecule be represented by m the momentum transferred at impact is $m(u - u')$ or $2m(u - w)$.

Again, if there are n molecules each having mass m and velocity u spaced uniformly along the length l perpendicular to the piston face, then the number of impacts on the piston that take place in the small interval of time δt is

$$\frac{n}{l}(u - w)\delta t,$$

and the total transfer of momentum in time δt is

$$2m \frac{n}{l}(u - w)^2 \delta t.$$

Further, if there are several groups of such uniformly spaced molecules having different values of n and u per group, the momentum transferred in time δt is

$$2m \delta t \sum \frac{n}{l}(u - w)^2.$$

We may next imagine, in addition, that there are N such lines of molecules (of velocity u) per unit area of face of the piston, and perpendicular thereto. Accordingly the transfer of momentum per unit area of piston face in time δt is

$$2m \delta t \sum \frac{nN}{l}(u - w)^2.$$

But the transfer of momentum per unit area in unit time measures the pressure p ; hence

$$p = 2m \Sigma \frac{nN}{l} (u-w)^2.$$

We observe that $\frac{nN}{l}$ is the number of molecules per unit volume of the cylinder having velocity u .

4. By assuming that all the molecules move perpendicularly to the face of the piston we have thus been able to sketch in a simple way the salient features of the problem.

Actually, however, the gas consists of molecules moving in many different directions and at many different velocities. Numerical estimates can, however, be made by the aid of Maxwell's law for the distribution of velocities in a mass of gas in a steady state. According to this hypothesis the number of molecules having a velocity component between u and $u + \delta u$ is equal to $ave^{-b^2u^2} \cdot \delta u$, where a and b are constants depending on the kind of the gas and on its density and temperature, and v is the total number of molecules per unit volume of the gas.

The theoretical pressure in this general case, in which the piston velocity is small compared with the mean molecular velocity in the gas, may be estimated by a method similar to that given in Sir J. H. Jeans's* 'The Dynamical Theory of Gases' for the determination of the pressure on a stationary plane surface. Thus let δS be an element of area of the piston face which is perpendicular to the direction of the velocity component u . Suppose the molecules to be divided into classes chosen so that all the molecules in one class have approximately the same velocities in magnitude and direction.

Let n_1, n_2, n_3 etc. be the numbers of molecules per unit volume of each class, and n be the number of molecules of all classes per unit volume, so that $n = n_1 + n_2 + n_3 + \dots$

Consider now one of the classes of molecules impinging in a shower on the piston face. Let u_1 be the velocity component perpendicular to the piston face of the

* Sir J. H. Jeans, 'The Dynamical Theory of Gases,' 4th edition, paragraph 146.

molecules of this class, and let the piston velocity be constant during the small interval considered and have magnitude w . The molecules of this shower which strike the area δS in the small interval of time δt will be those which, at the beginning of the interval, lie within a small cylinder having δS for base and height $(u_1 - w) \delta t$, and therefore of volume $(u_1 - w) \delta S \delta t$.

The number of these molecules is therefore

$$n_1(u_1 - w) \delta S \delta t,$$

and let the mass of each be m . The transfer of momentum perpendicular to the piston face by each of these molecules on impact is $2m(u_1 - w)$, so that the transfer of momentum in time δt due to the shower n_1 is

$$2mn_1(u_1 - w)^2 \delta S \delta t,$$

and for all the classes of molecules together the transfer is

$$2m \delta S \delta t \sum n_1(u_1 - w)^2,$$

the summation extending to all the molecules for which $u_1 - w$ is positive. This is equal to $p \delta S \delta t$; therefore

$$p = 2m \sum_w^{\infty} n_1(u_1 - w)^2.$$

We hypothesize that at the commencement of the interval the gas is in a steady state, and accordingly, on the Maxwell distribution, the number of molecules having the velocity component between u and $u + \delta u$ is

$$n = a v e^{-b^2 u^2} \cdot \delta u.$$

Now the most general steady state consists of a molecular motion compounded with a simple mass motion of the gas as a whole. We shall assume that the motion in the engine cylinder approximates to this for a short interval of time, and accordingly that the steady state persists for that interval. The motion of the gas in the cylinder is, in fact, turbulent, and at any instant the distribution of the velocities may be different from the Maxwell distribution.

As we are concerned with the comparison of the pressures when the piston is and is not in motion, we may, as an approximation, assume that the Maxwell distribution of velocities holds good approximately during the small interval of time under consideration. Moreover, as the

piston velocity is relatively small compared with the mean molecular velocity, this distribution will not be greatly departed from during the small interval of time. We shall suppose that the density of the gas during expansion is progressively reduced in a great number of stages, and suppose each stage to remain steady during the very short interval of time of its existence. Thus we may regard the results of estimates of the pressure as being a rough approximation throughout the whole of the expansion, and not merely applicable to the instant of time when the steady state is hypothesized. Substituting this value of n we obtain

$$p = 2ma\nu \sum_{w} e^{-b^2 u^2} (u-w)^2 \delta u.$$

Taking the interval δu indefinitely small and an exceedingly great number of molecules we have for the pressure the value

$$p = 2ma\nu \int_w^{\infty} e^{-b^2 u^2} (u-w)^2 du.$$

If the piston were stationary the corresponding value for the pressure p_0 is obtained by putting $w=0$ in this expression.

5. We have now to evaluate the integral in

$$p = 2ma\nu \int_w^{\infty} e^{-b^2 u^2} (u-w)^2 du.$$

As w is relatively small we can express the value of p conveniently in a rapidly converging series in the following way :—

$$\begin{aligned} & \int_w^{\infty} e^{-b^2 u^2} (u-w)^2 du \\ &= \int_0^{\infty} e^{-b^2 u^2} (u-w)^2 du - \int_0^w e^{-b^2 u^2} (u-w)^2 du. \end{aligned}$$

Now we know * that

$$\int_0^{\infty} e^{-b^2 u^2} du = \frac{\sqrt{\pi}}{2b},$$

* See Williamson's 'Integral Calculus,' 6th edition, Arts. 112, 116, 117; or Jeans' 'The Dynamical Theory of Gases,' 4th edition, Appendix A.

$$\int_0^{\infty} e^{-b^2 u^2} u du = \frac{1}{2b^2},$$

$$\int_0^{\infty} e^{-b^2 u^2} u^2 du = \frac{\sqrt{\pi}}{4b^3}.$$

Hence

$$\int_0^{\infty} e^{-b^2 u^2} (u-w)^2 du = \frac{1}{4b^3} \left\{ \sqrt{\pi} - 4bw + 2\sqrt{\pi}b^2w^2 \right\}.$$

To evaluate

$$\int_0^w e^{-b^2 u^2} (u-w)^2 du$$

we expand the exponential term.

Thus

$$e^{-b^2 u^2} = 1 - b^2 u^2 + \frac{b^4 u^4}{2} - \frac{b^6 u^6}{3} + \dots$$

Hence

$$\begin{aligned} \int_0^w e^{-b^2 u^2} (u-w)^2 du \\ = w^3 \left[\frac{1}{3} - \frac{1}{30} b^2 w^2 + \frac{1}{210} b^4 w^4 \right. \\ \left. - \frac{1}{1512} b^6 w^6 + \frac{1}{11880} b^8 w^8 - \dots \right], \end{aligned}$$

and accordingly

$$\begin{aligned} \frac{2b^3}{\pi a v} p = \sqrt{\pi} - 4bw + 2\sqrt{\pi}b^2w^2 - \frac{4}{3}b^3w^3 + \frac{2}{15}b^5w^5 \\ - \frac{2}{105}b^7w^7 - \frac{1}{378}b^9w^9 - \frac{1}{2970}b^{11}w^{11} + \dots \end{aligned}$$

Now if the piston be stationary we find the corresponding value of the pressure p_0 by putting $w=0$ in the above expression, so that

$$\frac{2b^3}{\pi a v} p_0 = \sqrt{\pi}.$$

Hence

$$\frac{p}{p_0} = 1 + 2b^2w^2 - \frac{4bw}{\sqrt{\pi}} \left[1 + \frac{1}{3}b^2w^2 - \frac{1}{30}b^4w^4 + \frac{1}{210}b^6w^6 - \frac{1}{1512}b^8w^8 + \frac{1}{11880}b^{10}w^{10} - \dots \right].$$

Now for a gas in a steady state devoid of mass motion the constant b is connected with the mean velocity c of the molecules (regardless of direction) by the relation

$$b = \frac{2}{\sqrt{\pi} \cdot c}.$$

Accordingly, if we put y for $\frac{w}{c}$ and reduce, we get

$$\frac{p}{p_0} = 1 - 2.546y + 2.546y^2 - 1.081y^3 + 0.138y^5 - 0.025y^7 + 0.0044y^9 - 0.00071y^{11} + \dots$$

6. But the piston, on account of its motion, not only experiences a diminution of pressure on one face, but also it is retarded by an increased pressure on the face towards the direction in which it is moving. The calculation of the increase of pressure due to the motion of the piston face towards a mass of gas proceeds similarly to that of the diminution of pressure due to the receding piston.

Here all the molecules with velocity components along the cylinder between $-\infty$ and $+w$ are involved, and by an exactly similar method of calculation it may be shown that the expression for the pressure is obtained by changing the signs of w and of y in the expression already found for p , the values of b and c being of course those appropriate to the gas on that face of the piston.

Thus

$$\frac{p'}{p_0} = 1 + 2.546y' + 2.546y'^2 + 1.081y'^3 - 0.138y'^5 + 0.025y'^7 - 0.0044y'^9 + 0.00071y'^{11} - \dots$$

Accordingly, on the kinetic theory, the pressure on the active face of the piston is somewhat lower than the gas would exert on a stationary piston, while the retarding or back pressure on the other face of the piston is somewhat

greater ; and the magnitudes of these differences depend on the piston speed.

7. As an alternative the following method may be employed ; it is based on the hypothesis that the gas may be regarded for the purpose of the investigation as complying with the following conditions :—

(a) All molecules which have the same total velocity are uniformly spread throughout the mass of gas.

(b) There is no priority of direction in regard to the motion of these molecules, *i. e.*, there are as many of these molecules of given velocity moving in one direction as another.

(c) The number of molecules per unit volume moving regardless of direction, with the resultant velocity between v and $v+dv$, follows the Maxwell distribution of resultant velocity, and is represented by

$$4\pi a^3 v e^{-\delta^2 v^2} dv.$$

Consider a mass of gas in contact with a flat plate which is moving with uniform velocity perpendicularly to its plane.

Imagine an element of area δS taken on the plane which coincides with the position of the plate at the commencement of the time during which the motion is considered.

Consider the molecules that move with velocity v and are contained in one parallel shower making an angle θ with the normal to the plate in its initial position and moving towards it, and let there be N such molecules per unit volume.

The number of linear streams per unit area is $N^{2/3}$ and the number of such streams of molecules that impinge on δS is $N^{2/3} \cos \theta \delta S$.

Each of these molecules exerts a momentum on the plate of $2m(v \cos \theta - w)$. The number of impacts per second per single line of molecules is $N^{1/3} (v - w \sec \theta)$. Hence the total momentum due to impact of the molecules of velocity v and direction θ is

$$2mN \cos^2 \theta (v - w \sec \theta)^2.$$

Thus we have obtained the pressure effect for the whole shower of molecules v, θ . We now proceed to find the

total effect for showers of molecules v from every possible direction.

Consider a hemisphere of unit radius round the centre of δS . We suppose the radius having direction θ to have concentrated along it the pressure effect measured by

$$2mN \cos^2 \theta (v - w \sec \theta)^2.$$

The ratio of the element of area on the hemisphere at any angle θ to its whole area is $\sin \theta d\theta$. Since there is no priority of direction and distribution in regard to numbers of molecules of velocity v , we presume an equal distribution all round the hemisphere, each direction θ , however, having its appropriate effect in producing pressure on δS .

Accordingly the total pressure on δS due to molecules of velocity v is obtained by integrating that due to each element, and is

$$2mN \int_0^{\cos^{-1} \frac{w}{v}} \sin \theta \cdot \cos^2 \theta \cdot (v - w \sec \theta)^2 \cdot d\theta.$$

The integration extends from $\theta=0$ to $\theta=\cos^{-1} \frac{w}{v}$, beyond which angle the molecules of velocity v do not reach the moving plate.

Hence the pressure due to molecules of velocity v is

$$\frac{2}{3} mN \frac{1}{v} (v-w)^3.$$

Now since for each direction θ and velocity of molecule v we are concerned only with those molecules travelling towards δS , and not with those travelling away from it, the number N is half the whole number of molecules having velocity v .

Hence

$$N = 2\pi a^3 v e^{-b^2 v^2} \cdot v^2 \cdot dv$$

on Maxwell's distribution of resultant velocity v . Hence the pressure due to all velocities between w and ∞ is

$$p = \frac{4\pi}{3} m a^3 v \int_w^\infty e^{-b^2 v^2} \cdot v \cdot (v-w)^3 \cdot dv.$$

This integral may be evaluated by expansion in a manner exactly similar to that employed in paragraph 5.

Observing that $\sqrt{\pi}.a=b$, we obtain as a result the same values of $\frac{p}{p_0}$ and $\frac{p'}{p_0}$, as those already found in paragraphs 5 and 6, a result which may also be established by examination of the integrals in question.

8. Problems in the kinetic theory of gases are sometimes solved with rough approximation on the assumption that all the molecules travel with the same velocity, and in order that the pressure produced and the kinetic energy shall be the same as for the gas this common velocity is the square root of the mean of the squares of the individual molecular velocities. If this velocity be represented by q , then for a gas in a steady state it is well known * that

$$q = \sqrt{\frac{3\pi}{8}}.c = 1.086 c,$$

where c is the mean velocity of the molecules.

As an alternative to the Maxwell distribution of velocities of paragraph 7 we shall suppose all the molecular velocities to be the same in magnitude and equal to q .

As in paragraph 7 we find that the total pressure p

is
$$\frac{1}{3} m \nu \frac{1}{q} (q-w)^3,$$

where ν is the total number of molecules per unit volume. Hence

$$p_0 = \frac{1}{3} m \nu q^2.$$

Since

$$\sqrt{\pi}.a=b \text{ and } q^2 = \frac{3\pi}{8} c^2 = \frac{3}{2b^2},$$

it is seen that this value of p_0 agrees with that given in paragraph 5.

Then

$$\begin{aligned} \frac{p}{p_0} &= 1 - 3 \frac{w}{q} + 3 \frac{w^2}{q^2} - \frac{w^3}{q^3} \\ &= 1 - 2.765 y + 2.546 y^2 - 0.782 y^3, \end{aligned}$$

since

$$w = cy \text{ and } q = 1.086 c.$$

* See Sir J. H. Jeans, 'The Dynamical Theory of Gases,' 4th edition paragraph 30.

When the plate is moving towards the gas we have

$$\frac{p'}{p_0} = 1 + 2.765y' + 2.546y'^2 + 0.782y'^3.$$

9. It may be worth recording the results of estimates made on other hypotheses, although susceptible of less accuracy.

(a) Suppose that, while all the molecules of the gas contained within a cube have the same velocity q , one-sixth of the total number are moving perpendicularly towards each face of the cube at the time considered.

The plate being parallel to one face of the cube there are now $\frac{1}{6}\nu$ molecules involved in impingement on the plate, and the pressure is

$$p = \frac{1}{3}m\nu(q-w)^2$$

and

$$p_0 = \frac{1}{3}m\nu q^2 \text{ as in paragraph 8.}$$

Hence

$$\begin{aligned} \frac{p}{p_0} &= 1 - 2\frac{w}{q} + \frac{w^2}{q^2} \\ &= 1 - 1.842y + 0.848y^2. \end{aligned}$$

Also

$$\frac{p'}{p_0} = 1 + 1.842y' + 0.848y'^2.$$

(b) Suppose that at the time considered the molecules have equal components of velocity in a direction normal to the plate, half the total number moving towards the plate and half away from it. Let this common velocity component be u and let $u^2 = \frac{1}{3}q^2$.

Then, since $\frac{1}{2}\nu$ molecules are involved,

$$p = m\nu(u-w)^2$$

and

$$p_0 = m\nu u^2 = \frac{1}{3}m\nu q^2 \text{ as before.}$$

$$\begin{aligned} \frac{p}{p_0} &= 1 - 2\frac{w}{u} + \frac{w^2}{u^2} \\ &= 1 - 3.192y + 2.546y^2. \end{aligned}$$

Also

$$\frac{p'}{p_0} = 1 + 3.192y' + 2.546y'^2.$$

The foregoing results are contrasted in the following table :—

Paragraph..	Value of $\frac{p}{p_0}$.				Value of $\frac{p'}{p'_0}$.			
	5.	8.	9 (a).	9 (b).	6.	8.	9 (a).	9 (b).
<i>y</i> or <i>y'</i> .								
·01	·975	·973	·982	·968	1·026	1·028	1·018	1·032
·05	·849	·868	·912	·847	1·134	1·145	1·094	1·166
·1	·770	·748	·824	·706	1·281	1·303	1·193	1·344
·2	·584	·543	·665	·464	1·620	1·661	1·402	1·740
·5	·233	·156	·291	·040	3·041	3·117	2·133	3·230

10. The numerical value of the mean molecular velocity *c* for different gases at 0° C. may be got from tables of physical constants*.

For a given gas the mean molecular velocity is proportional to the square root of its absolute temperature. Accordingly its value may be deduced for any temperature *t*° C. by multiplying the tabulated figure for 0° C. by

$$\sqrt{\frac{273+t}{273}}.$$

For different gases the corresponding values of *c* are inversely proportional to the square root of the molecular weight.

For oxygen *c*=42,500 cm. per sec. at 0° C.

If *W* be the molecular weight of a gas and *t*° C. be its temperature,

$$\begin{aligned} c &= 42500 \sqrt{\frac{32(273+t)}{273 W}} \text{ cm. per sec.} \\ &= 14500 \sqrt{\frac{273+t}{W}} \text{ cm. per sec.} \end{aligned}$$

11. As a numerical example take steam at 200° C. on one side of the piston and at 50° C. on the exhaust side, and let the piston speed at the particular instant considered be 1000 cm. per sec.

Then, since *W*=18, *t*=200, and *t'*=50, we find *c*=74200, *c'*=61500 cm. per sec.

* See Jeans, *ibid*, paragraph 151; or Kaye and Laby, 'Physical and Chemical Constants.'

Hence $y=0.0135$, $y'=0.0163$.

Accordingly, by the formulæ of paragraphs 5 and 6,

$$\frac{p}{p_0}=0.9660, \quad \frac{p'}{p_0}=1.0423.$$

If now $p_0=225$ lb./sq. in., and $p_0'=1.8$ lb./sq. in., therefore

$$\frac{p-p'}{p_0-p_0'}=\frac{217.35-1.88}{225-1.80}=0.965.$$

Thus, according to the kinetic theory and on the assumptions made, the effective pressure on the piston in this example is about $3\frac{1}{2}$ per cent. less than that due to the steam and exhaust pressures regarded as acting on a stationary piston. If the indicator stroke is, say, one-tenth of the piston stroke, the kinetic effect upon it can in like manner be calculated, and it will be found that the indicator gives an effective pressure in this example about $3\frac{1}{4}$ per cent. greater than that experienced by the piston.

The assumption that the working substance is in a steady state at a particular moment may not be exactly realized; it is used here chiefly as a basis for estimating the comparative pressures on the piston and plunger under like and theoretically manageable conditions.

12. It is of interest to compare the results arrived at in paragraphs 5 and 6 for the pressure on a piston moving in a closed cylinder with the pressure on a flat plate moving in a normal direction through the open air as found by experiment.

In the latter case the air streams along the surface of the plate and past its edges, and as a consequence the pressure upon it is probably not uniform and is everywhere less than if the gaseous stream was reflected entirely normally. Moreover the air stream, on getting round to the back of the plate, exerts some pressure thereon. On the other hand, the gas reacting on the piston is prevented by the cylinder walls from escaping in this way, and it may therefore be expected to exercise more effectively its molecular bombardments with consequent greater pressure on the front face and lower pressure on the back face. Now for moderate velocities of a flat plate moving in a normal direction in the air

the resultant pressure per unit area, taking into account the action on both faces, is found by experiment to be connected with the velocity approximately by a relation of the form $P = kv^2$, where k is approximately 1.05×10^{-5} when P is measured in pounds weight per square inch and v in feet per second.

From paragraphs 5 and 6 for air in a steady state, if we take p_0 the same for both faces, we find the resultant pressure $p' - p$ is given by

$$\frac{p' - p}{p_0} = 5.092y + 2.162y^3 - 0.276y^5 + \dots$$

Now for air at 15°C. the mean molecular velocity c is approximately 1500 ft. per sec. Also $p_0 = 14.7$ lb. wt. per sq. in.

Hence follows the comparative table :—

v , ft./sec.	y .	$\frac{p' - p}{p_0}$.	$p' - p$, lb./sq. in.	P , lb./sq. in.
15	.01	0.051	0.75	0.0024
75	.05	0.255	3.75	0.0591
150	.10	0.511	7.53	0.2362
300	.20	1.037	15.24	0.9450
450	.30	1.587	23.33	2.126
600	.40	2.173	31.94	3.780
750	.50	2.809	41.29	5.906

It thus appears that the conditions assumed in paragraphs 5 and 6 as to the working substance in the engine cylinder lead to resultant pressure differences on the opposite faces of the piston that are much higher than the corresponding pressure differences on a plate moving in the open air, particularly at very low velocities. This disparity between the results in the two cases may perhaps be explained wholly or largely by the differences outlined above between the physical conditions in the two cases. Possibly the assumptions made in regard to the action on the piston are not entirely justifiable and lead to too high values of the pressure. At any rate, it appears to be desirable to carry out experiments to determine to what extent the pressure on the piston when it is in rapid motion differs from that exerted upon it when it is at rest.

XII. *Studies on the Oxidation of Metals.*—Part I.

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[Plates V. & VI.]

SUMMARY.

OXIDE films formed on lead and tin have been examined by the electron diffraction method. The films have been studied at room temperature by removing them from the molten metal on wire loops and by preparing them by heating foils supported on wire loops. Photographs have also been obtained of the films formed on molten drops of these metals at temperatures a little above their melting-points. The oxide films of tin yield diffraction photographs characteristic of the usual SnO_2 structure—a tetragonal cell of side 4.72 \AA. and height 3.17 \AA. Traces of SnO are possibly present, and the SnO_2 film is probably orientated with the “ c ”-axis perpendicular to the surface of the drop. The oxide films of lead prepared by heating foil and by removing the oxide from the molten metal consist of orthorhombic (yellow) PbO , with possibly traces of the tetragonal (red) modification. They show orientation with the “ c ”-axis perpendicular to the plane of the film. The oxide film on drops of molten lead is tetragonal (red) PbO ; orientation of these films has not been detected.

Introduction.

THE experiments described below have been undertaken in connexion with a research proceeding in the Metallurgy Department into the formation of oxide films on molten metals. Interest was primarily focussed on the pellicle formed when a clean molten metallic surface is first exposed to the action of oxygen. The electron diffraction method appeared to offer a way of obtaining information about the structure of these films, and the work has been carried out with a view to exploring the possibilities of the method in this field.

Considerable difficulties have been encountered in obtaining diffraction photographs from the surfaces

* Communicated by Sir J. E. Petavel, K.B.E., D.Sc., F.R.S.

of the molten metals examined, although the apparatus was capable of giving photographs, by transmission through thin films, of sufficient perfection and accuracy for the present purpose. Examples of these are reproduced in Pl. V. fig. 3 and Pl. VI. fig. 5, and are described below. Photographs by reflexion from the surface of a solid have been obtained, but require much longer exposures; the lines, however, are usually measurable with an accuracy not very much less than in the case of the transmission photographs. The calibration photograph of zinc oxide (Pl. V. fig. 2) shows that this material, deposited on a copper wire, gives very good results. As the conditions here are geometrically similar to those obtaining in the case of an oxide film formed on the curved surface of a molten drop it is clear that the comparatively poor results obtained from the drop are ascribable to the form of the oxide layer, and not to any imperfection in the instrument. The most obvious physical difference between the surface of a molten drop and that of an oxide "smoke" condensed on a wire (or on an optically smooth solid surface) is in the degree of roughness. It seems possible that the photographs of the smoke are in reality "transmission" photographs, the electron penetrating small particles of oxide projecting from the surface*. Effects due to refraction of the electron waves would not arise in such circumstances. The surface of the metal drop, however, is smooth on an atomic scale, and effects due to refraction at the small angles of incidence used may require to be taken into account if this smoothness is communicated to the oxide layer by the metal. The difficulty of obtaining good photographs from the films on molten metal surfaces may be due to some such cause, but the accuracy with which the diameters of the rings are measurable is not, unfortunately, sufficiently good to afford any numerical test. No account has therefore been taken of any effect due to refraction in the oxide film in the evaluation of the results obtained from the molten drops.

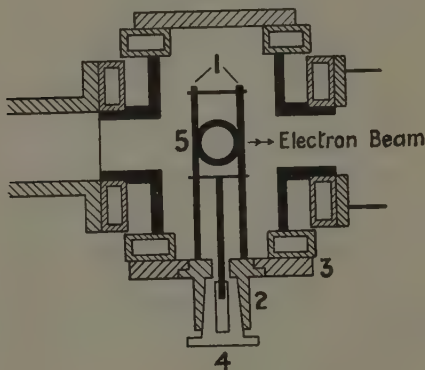
Apparatus.

The electron diffraction apparatus used in the present investigation differs only in minor details from equipment

* G. P. Thomson, 'Wave Mechanics of Free Electrons,' p. 158 (1930).

used and fully described by previous investigators. The only novelty is the introduction of a section to accommodate a small furnace, so that diffraction photographs could be obtained from the surface of molten drops of metal. The furnace chamber (fig. 1) is built up from brass tube of 7 cm. diameter with smaller tubes 3 cm. diameter soldered on to it. The tubes are provided with water-cooled flat end plates as shown in the diagram. The furnace is carried on a steel sheet through holes in which pass two silica tubes (1) mounted on steel rods screwed into the disk (2). The furnace is thus thermally insulated from the supports and is free to slide along them.

Fig 1.



The motion is imparted to it by means of the conical ground-joint, into which is threaded a rod attached to the furnace mounting. The whole furnace can be removed from the apparatus by breaking the waxed joint which holds the disk (2) into the larger circular plate (3). The latter is greased and allows the furnace to be adjusted as to height until the electron beam just grazes the surface of the molten drop. By manipulation of the conical joint (4) the drop is adjustable horizontally, so that its summit may be brought into the path of the electrons. The other opening to the furnace chamber is closed by a sheet of plate glass, through which the drop can be observed, and which is easily removable for changing the specimen when required. The furnace

itself (5) consists of a disk of mild steel the upper surface of which is machined concave to hold the drop of molten metal. The heating element is a length of "bright ray" wire of approximately 8 ohms resistance closely wound into a helix about 3 mm. diameter; about four turns of this helix are wound on a silica tube 1 cm. diameter and 2 cm. long, and over the winding is fitted another silica tube 2 cm. diameter. A steel screw passes through the inner tube, engages in a threaded hole in the disk which forms the top of the furnace, and holds the silica tubes in place. The leads to the winding are led out through holes in the disk (2). Provision for thermocouple leads for temperature measurement was also made, but in the present investigation these have not been used. A current of 1.2 amperes in the winding was sufficient to maintain a drop of lead molten in the vacuum.

The high tension supply was derived from a 2 kv.a. transformer, capable of an output of 64 kv. peak, supplied from the 220 volt 50 cycle mains. The discharge-tube rectified efficiently, and no smoothing equipment was used. A voltage measuring device was included in the high tension equipment. This consisted of a high resistance, 100 megohms nominal, and a rectifying microammeter (Ferranti) in series, both in parallel with the discharge-tube. The resistance was built up from twenty-five 4 megohm resistances (Siemens-Hochkonstantwiderstände) assembled in series in a pyrex tube filled with transformer oil. The microammeter scale reading was then calibrated against diffraction photographs of zinc oxide smoke deposited on copper wire (Pl. V. fig. 2), the de Broglie wave-length of the electron beam being calculated from the measurements of the diffraction pattern, assuming that ZnO has a hexagonal structure $a=3.25 \text{ \AA.}$, $c=1.61$. As an example, when the tube was run so that the microammeter scale reading was 375, measurement of a photograph of ZnO showed that a wave-length of 0.0522 \AA. would lead to the required parameter. This wave-length corresponds with a voltage of 52.5 kv., which is quite close to the value $100\sqrt{2} \cdot 375 = 53.1 \times 10^3$ which would be obtained by assuming that the resistance actually had its nominal value and that the voltage wave was sinusoidal. Experiments of this kind showed that the values of spacings derived from the best photographs can be relied on to an accuracy

of about ± 2 per cent. In a series of measurements of one plate the different spacings will yield values of the parameters of the ZnO cell which agree with one another to a higher accuracy. For instance, in one photograph the lines were measured by a ruler, and a value of the side of the cell was calculated from each diffraction line. The maximum divergence from the mean of all the values so obtained was $\pm 0.02 \text{ \AA.}$, while the mean divergence (*i. e.*, the arithmetic mean of all the differences) for twenty rings measured was less than 0.01 \AA. , representing an error of just 0.3 per cent. With two exceptions all the photographs of which measurements are given in Tables I., II., and III. were taken under the standard conditions referred to above, namely, a scale reading of 375 microamps, and the wave-length has been assumed to be 0.0522 \AA. in computing the spacings. The two exceptions are the results given in Table III. columns (a) and (b). These photographs were taken with a scale reading of 350 microamps, and the voltage has been taken to be $100\sqrt{2} \ 350 = 49.5 \text{ kv.}$, corresponding to a wave-length 0.0537 \AA.

Experimental Procedure.

Sufficient metal, cleaned chemically or by scraping, was placed on the surface of the furnace to form when melted a drop from 1 to 2 centimetres in diameter. After sealing off the system the pressure was reduced to under 10^{-3} mm. of mercury (measured by an ionization gauge) before switching on the furnace heating current. The effect of switching on the current was usually to produce a temporary rise of pressure, but the gases emitted during heating were generally so quickly removed by the pumps that fusion could be carried out at pressures at or even slightly below 10^{-4} mm. of mercury. The current to the high voltage transformer was then switched on and the pressure in the discharge-tube adjusted by means of a needle-valve until the tube was operating at the required voltage. The electron beam is visible as an intense spot on the fluorescent screen provided it is not obstructed by the molten drop of metal. To obtain a photograph the whole furnace is raised by sliding the plate (3) (fig. 1) upwards on the furnace chamber until the electron beam as seen on the screen is partly obscured. The desired exposure is then made.

Oxidation of the specimen at low pressures was carried out by allowing air to accumulate in the discharge-chamber and force its way through the apertures, air dried by passing through calcium chloride being used. Pressures up to 10^{-3} mm. could be measured by the gauge, and most of the oxidations have been carried out at about this pressure. In those cases where higher pressures have been used the heating of the diffusion pumps was temporarily stopped and air admitted to nearly atmospheric pressure.

Results.

1. Tin.

Oxide films on tin, prepared by oxidizing a sheet of tin-foil in a flame, have been examined by Bragg and Darbyshire *, who found that the film yielded an electron diffraction spectrum characteristic of a body-centred tetragonal unit with side $a=4.72$ Å. and height $c=3.17$ Å., identical with the unit of SnO_2 . This result has been confirmed by examination of material prepared by fusing a small sheet of tin-foil mounted on a loop of copper wire and of a specimen obtained by drawing a film from the surface of molten tin on to a wire loop. The measurements of two photographs, one of which is reproduced in Pl. V. fig. 3, yielded the results given in Table I. columns (i.) and (ii.). Of these column (i.) refers to the specimen obtained on a wire loop from the surface of the molten metal. The photograph was measured up on a recording photometer, and comparison of the observed spacings with those calculated from the results of an X-ray examination of SnO_2 shows good agreement. The figures included in column (ii.) were obtained from a photograph of a specimen of foil heated in a flame, and are in fairly good agreement with the calculated spacings. Both these photographs show one weak ring, spacing 2.15 Å., which does not belong to the SnO_2 structure. The measurement of photographs obtained from the surface of molten drops of metal gave the results included in columns (iii.) to (vi.) of Table I.

The specimen responsible for the results in column (iii.) was freshly cut from a block of metal, scraped and washed in acetone. It was melted in the "rough" vacuum

* Trans. Faraday Society, xxviii. p. 522 (1932).

and then allowed to oxidize for a few minutes at nearly one atmosphere of air. Five photographs were taken with the specimen in different positions; all showed the same set of rings (Pl. V. fig. 4), of which those given in the table are typical. The values of " d " are larger than those calculated from the X-ray data, but this is doubtless due to the use of a wrong value for the voltage in the evaluation. One ring, spacing 3.05 \AA. , is not accounted for. Column (iv.) refers to a photograph of the same specimen which, after solidification, was scraped and replaced in the apparatus. It was melted in the rough vacuum, and the photograph yielded the values given in the table. It was then left molten in the rough vacuum for $2\frac{1}{2}$ hours, the photograph after this treatment showing faint rings which seem to be identical with those in the table. After further oxidation at 1 atmosphere of air the photograph still showed rings; although these are rather faint they appear to correspond with those already obtained. On all the photographs of this specimen the rings are granular, as if due to rather large grains of oxide. A new specimen of tin, melted in the rough vacuum and oxidized for a few minutes at about half an atmosphere's pressure of air, gave a photograph of which the results are recorded in column (v.). No change in the rings was observed after leaving the metal molten in the rough vacuum for two hours. The rings are again granular, and one of them is reduced to a small arc indicating orientation of the film. The measured spacing of this ring is 1.67 \AA. , and is equal to the spacing for the plane (220) calculated from X-ray data. If these indices are assigned to this ring the calculated value of " a " becomes 4.72 \AA. , while the remaining rings on the photograph yield a mean value of 4.86 \AA. If the indices (002) are assigned to the ring the value of " a " is 4.99 \AA. The divergence from the mean is still so large that it is impossible to draw any definite conclusion as to which of these planes is parallel to the surface of the drop.

The figures in column (vi.) refer to the same specimen after cleaning with hot concentrated hydrochloric acid. The metal was melted at a pressure of less than 10^{-3} mm. of mercury, and the drop appeared to be very clean and mobile. A photograph obtained from the drop in this condition yielded the results under (vi.) in the table.

The rings are again granular and the spacing 2.97 \AA . again appears. Oxidation of the drop for five minutes in the rough vacuum produced no change in the diffraction pattern, although the oxide film was visible as a dulling of the surface of the metal, and the drop had lost its mobility. Further oxidation for five minutes at a pressure of about 1 mm. produced no change. All the photographs of this drop showed a marked streak on the plate perpendicular to the surface of the drop. This streak is connected in some way with the impact of the electron beam on the surface of the metal, because in another series of photographs in which exposures were made with the specimen lowered just out of the beam the streak was not present, but appeared in conjunction with rings when the specimen was raised into the beam. In one or two cases in which longer exposures have been given a second streak parallel to the first but less intense is present. A similar effect has been observed with some drops of molten lead (Pl. VI. fig. 6).

From the observations described above we may conclude that the comparatively thick films formed on the surface of molten tin at atmospheric pressure and removed for examination consists largely of SnO_2 , with the usual body-centred tetragonal structure of this material. The rings in the transmission photographs show no sign of breaking up into arcs due to orientation of the crystals, but, on the other hand, no ring corresponding to indices (002) is recorded. This particular reflexion in X-ray photographs of powdered SnO_2 is quite intense, so its absence from the electron diffraction photographs may possibly be due to orientation of the crystals in such a way that the basal plane (001) is approximately parallel to the surface of the film. The uniformity of the rings from other planes indicates that the orientation about the normal to the surface is random. Some support is lent to this view by the results obtained from the surfaces of molten drops. In three cases a ring corresponding to reflexion from (002) planes is observed, and in one a ring which may have these indices assigned to it is reduced to a short arc, showing orientation of this plane parallel to the surface of the metal. The relative weakness of the reflexions (110) and (200) is also consistent with this view. This inference is subject to a reservation with regard to the certainty with which the spectra obtained from the films

TABLE I.

X-ray SnO ₂ .		(i.)		(ii.)		(iii.)		(iv.)		(v.)		(vi.)		SnO.	
<i>hkl.</i>	d (calc.).	I.	d (obsd.).	I.	d (obsd.).	I.	d (obsd.).	I.	d (obsd.).	I.	d (obsd.).	I.	d (obsd.).	d (calc.).	<i>hkl.</i>
110	3.34	vs	3.32	vs	3.46	m	3.40	w	3.40	w	3.40	w	3.40
..	m	3.05	w	2.80	..	2.97	m	2.97	2.96	101
101	2.64	m	2.65	vs	2.73	m	2.64	w	..	w	2.64	w	2.64	2.67	110
200	2.36	s	2.34	s	2.40	w	2.47	w	2.47	w	2.47	2.38	002
..	..	w	2.18	w	2.15	1.88	200
211	1.76	vs	1.74	vs	1.80	s	1.80	m	1.82	m	1.83	s	1.83	1.78	112
220	1.67	w	1.70
002	1.59	w	1.65	m	1.67	m	1.64	1.59	211
310	1.50	m	1.49	ms	1.50	w	1.54	m	1.54	m	1.53	1.48	202
112	1.43	m	1.41	s	1.44	1.46	103
301	1.41	w	1.46
202	1.32	1.33	220
321	1.21	w	1.20	..	1.24	w	1.22	w	1.25	1.21	301
400	1.18	w	1.16	m	1.17	1.19	004
222	1.15	mw	1.08	ms	1.10	w	1.10	w	1.08	1.16	114
330	1.11														
312	1.09														
411	1.08														
420	1.06	1.06	312
103	1.03	1.02	321
402	0.948	m	0.97	w	0.95
213	0.912	m	0.92
510	0.912	w	0.905	m	0.92
332	0.907
431	0.907
501	0.907
α		4.70±0.01	4.84±0.03	4.84±0.03	4.84±0.03	4.78±0.03	4.88±0.03	4.87±0.06	4.87±0.06	4.86±0.06	4.86±0.06	4.86±0.06	4.86±0.06	3.77	3.77
αc		3.15	3.24	3.24	3.24	3.20	3.27	3.26	3.26	3.25	3.25	3.25	3.25	4.77	4.77

on molten drops can be identified with that to be expected from SnO_2 . In view of the difficulty of obtaining photographs which could be accurately measured the numerical agreement is perhaps as good as could be expected, but the presence of an extra line both in the "transmission" and "reflexion" experiments suggests that other structures may be present. The spacing 3.00 \AA . may be the line (101) in the spectrum of SnO^* of which the calculated spacing is 2.95 \AA . The spacings of SnO are given in the last column of Table I. It will be seen that the spectrum of SnO_2 differs from that of SnO only in the spacing of the first line. The figures in columns (i.) to (vi.) indicate that the film on the molten tin is SnO_2 , but in three cases there may be SnO present as well, a result in agreement with some recent observations by Steinheil †.

One further point deserves mention. It has not been found possible to produce a molten drop of metal which did not show diffraction rings, although in some cases they have been very feeble. Observations made on small polyhedral lumps of metal melted in a vacuum of 10^{-3} mm. of mercury or less show that the drop has oxide present on its surface. In some cases small polygonal patches of dullness on its surface are clearly the outline of the original facets of the polyhedral lump. These films differ mechanically from those produced by oxidation of the molten drop, because the drop as melted, even when patches of oxide film are visible, is quite mobile, a slight tap on the apparatus serving to throw it into violent oscillation. When, however, air is admitted to a pressure of about 0.01 mm. of mercury the drop in a few seconds stiffens, so that a moderately violent blow on the end of the camera fails to move it—in fact, the drop appears to be quite solid. It seems probable that the difference lies in the continuity of the film. When the polyhedron melts into a drop the oxide on the surface is ruptured and floats on it in discontinuous patches. It is these patches, the remains of the oxide film formed at room temperatures, which give rise to the rings observed from the drop immediately after fusion. When air is admitted, even at low pressure, the first effect on the drop is to form a thin continuous film of

* Levi, *Nuovo Cimento*, i. p. 335 (1924).

† *Ann. der Physik*, xix. p. 465 (1934).

solid oxide which effectively reduces its mobility, but does not, so far as we have observed, alter the nature and in some cases the intensity of the diffraction pattern.

2. Lead.

Bragg and Darbyshire * have examined films of lead oxide by the electron diffraction method, and obtained a spectrum which was interpreted as showing the presence of PbO_2 . The specimen was prepared by withdrawing a thin film on a copper-wire loop from the surface of molten lead. In the present investigation films prepared in this manner, and also by the fusion (in a Bunsen flame) of thin lead-foil supported on a copper-wire loop, have been examined (Pl. VI. fig. 5). Both types of material yielded the same spectrum, but this appears to differ from that obtained by Bragg and Darbyshire and to be yellow orthorhombic PbO . Table II. contains a list of the spacings observed from photographs of these two specimens, and it will be seen that there is very good agreement with the X-ray results of Halla and Pawlek †. With the exception of the first two rings and a ring of spacing 1.41 Å. all the intense lines of the X-ray spectrum are present in the electron diffraction spectrum, and many of the reflexions of medium intensity are also observed. The photograph obtained from the film of oxide withdrawn from the surface of the molten lead on a wire loop was measured by means of a travelling microscope; the values of " d " calculated from the diameter of the rings were all about 2 per cent. higher than the X-ray values. For purposes of comparison therefore these figures have been multiplied by a factor 0.98, in order that the agreement may be made clear at a glance. This means that the parameters of the orthorhombic cell, calculated from the electron diffraction data, will in this case be 2 per cent. larger than those obtained by Halla and Pawlek. The difference is well within the errors which are possible, and may be ascribed to an incorrect measurement of the voltage of the electron beam and to some inaccuracy in the figure (34.5 cm.) assumed for the distance from specimen to photographic plate. In the column of figures for the photograph obtained from foil

* *Loc. cit.*

† *Zeit. für phys. Chemie*, cxxviii. p. 49 (1927).

TABLE II.

X-ray (Halla and Pawlek).			Film from melt.		Fused foil.	
<i>hkl.</i>	<i>d.</i>	I.	<i>d</i> × 0.98	I.	<i>d.</i>	I.
001	5.88	m	4.01	m	4.09	w
110	3.58	w				
..	3.13	vs	3.21	vs
111	3.06	s	3.06	vs	3.08	vs
002	2.95	vs	2.95	vs
200	2.75	m	2.73	vs	2.77	s
201	2.49	vw	2.49	w	2.50	vw
020	2.37	m	2.37	s	2.40	s
112	2.27	vw	2.20	w	2.25	m
202	2.01	s	2.03	w	2.07	s
003	1.95	m	1.90	m
022	1.84	s	1.84	s	1.86	m
220	1.79	m	1.79	s	1.76	w
113	1.72	s	1.73	w		
310	1.71
311	1.64	s	1.65	vs	1.68	s
203	1.60	vw	1.53	s	1.56	w
222	1.53	s				
023	1.51	w				
131	1.47	s	1.47	m	1.50	vw
004						
..	1.41	mw	1.44	vw
400	1.38	vw
114	1.36	m	1.37	mw	1.36	vw
223	1.32	w	1.32	w	1.32	m
104	1.29	s	1.28	w	1.28	w
313						
024	1.25	m	1.24	m	1.23	m
402	1.24	w
133	1.20	m	1.20	s	1.20	m
330	1.17	w
005	1.16	m	1.17	s	1.16	vw
040						
331						
224	1.13	1.12	m
115	1.11	s	1.10	m		
314						
042	1.10	w
422						
240	1.09	w	1.09	..	1.09	w
205	1.08
134	1.05	m	1.05	m	1.05	w
511						
025						
333	1.03	m	1.03	m		
512	1.00 ₆	w	1.02
			1.01	..		
404	m	1.00	w

fused in a Bunsen flame the values of "*d*" are those obtained from measurement of the plate by means of a steel rule divided into a scale of 0.5 mm.; the measurements are not quite so precise, but the values of "*d*" fall nearer the X-ray result.

These two results are sufficient to show that for films prepared in the manner described the structure is that of orthorhombic (yellow) PbO. The values of the parameters of the unit cell containing four molecules of PbO are, according to Halla and Pawlek,

$$a=5.50\pm0.02 \text{ \AA.},$$

$$b=4.72\pm0.03 \text{ \AA.},$$

$$c=5.880\pm0.003 \text{ \AA.},$$

and the electron diffraction photographs yield a result agreeing with this within 2 per cent. With regard to the lines observed in the electron diffraction photographs and not in the X-ray diffraction spectrum it may be observed that one of these, spacing 4.01, might have assigned to it the indices (101); the other two do not appear to have any place in the structure of yellow PbO. The possibility of contamination of the specimen during preparation must be borne in mind, so that it does not appear justifiable to base any conclusions on the presence of these lines unless some independent evidence as to their source can be obtained.

One noteworthy feature of both the transmission photographs is the way in which the rings are broken up into arcs, indicating a fairly well marked orientation of the crystals in the oxide film. As a result of this the intensities of the rings recorded in the table have little significance, because the plates were measured up in different directions, and rings which did not appear in one series of measurements appear in another quite strongly. In a structure of the complexity of that with which we are here dealing the breaking up of the rings into arcs is an advantage, as it effectively increases the resolving power of the method. Rings the radial separation of which might be so small as to cause overlapping are separated on the plate by displacement circumferentially.

In contrast with the transmission photographs, so conspicuously rich in lines, the spectra obtained by reflexion from the surfaces of molten drops of lead consist

of comparatively few rings. The spacings corresponding to the rings in eight different photographs are listed in Table III., (a) to (b), and for purposes of comparison the table includes in the left-hand columns the results obtained by Levi * from an X-ray examination of tetragonal (red) PbO. The values of " d " have been calculated from the data given by Darbyshire †, namely, $a=3.968 \text{ \AA}$. and $ac=5.011 \text{ \AA}$. The following is a brief description of the conditions under which the electron diffraction spectra were obtained:—

Table III. (a). A piece of lead cleaned with nitric acid melted in the apparatus. It was visibly not clean after fusion, and gave rings in a photograph taken immediately after fusion had occurred. The drop was then oxidized by the admission of air to a pressure of about 0.1 mm. of mercury; photographs were taken in two different positions of the drop; both showed rings, from which the figures in the table under (a) were obtained. Further oxidation under similar conditions produced no change in the ring system.

Table III. (b). The same piece of lead cleaned by scraping; it melted (*in vacuo*) with small patches of oxide floating on the surface. The photograph in this condition showed rings with spots. The drop was then oxidized until extreme mobility ceased, and yielded the spectrum recorded in the table. Further oxidation until the surface became a little dull produced no change in the ring pattern.

Table III. (c). A fresh piece of lead melted (*in vacuo*) gave a good ring pattern, of which the results are recorded in the table. Further oxidation for periods of two to four minutes at a pressure of about 0.1 mm. produced no change. The figures in the table are in very good agreement with the X-ray spectrum of tetragonal (red) PbO.

Table III. (d). The same specimen, cleaned with nitric acid and re-melted. It appeared very clean on fusion, but gave a ring pattern. Oxidation for two minutes reduced the mobility of the drop, and a photograph in this condition yielded the results in the table. It was noticed that the drop appeared to recover its mobility to some extent when left standing in the vacuum.

* *Nuovo Cimento*, i. p. 335 (1924).

† *J. Chem. Soc.* p. 211 (1932).

Table III. (*e*). The same drop not cleaned melted in air at a pressure of 1.6×10^{-4} mm. of mercury (Pl. VI. fig. 6).

Table III. (*f*). A fairly thick film produced by admitting air to the apparatus, with the specimen molten, to a pressure of nearly an atmosphere.

Table III. (*g*). A fresh specimen of lead melted at 3×10^{-4} mm. pressure. Photographs, as melted, gave a series of broad rings not easily measurable, but apparently identical with those previously observed from other specimens. The drop was oxidized for five minutes at about 0.1 mm. pressure, and yielded the spectrum in the table.

Table III. (*h*). A thick film produced by allowing air to pass over the molten specimen. Broad rings, difficult to measure.

Inspection of the figures in Table III. shows that there is remarkably close agreement between the observed values of the spacings and those to be expected from the tetragonal cell of red PbO. Such a conclusion must, however, be accepted only after a critical examination of the experimental data. Comparison of Tables II. and III. shows that every spacing of the tetragonal structure is represented very closely by a spacing in the orthorhombic. If, however, the film on the molten lead is orthorhombic oxide, it becomes necessary to explain the absence of a number of strong rings observed in the transmission photographs. The rings in the reflexion photograph within the limits of the strip observed (and this includes 180° for the inner rings) do not show any sign of orientation. Two of the missing rings have indices (002) and (020), so that it is difficult to suggest any type of orientation which would produce the desired effect. Moreover the ring (002) of spacing 2.95 Å. should be separated from the first line of the tetragonal structure (101) spacing 3.11 Å. by 0.5 mm., and would be resolved in some of the photographs if present. The conclusion therefore that the film on the molten lead is tetragonal (red) PbO seems the most natural*, and it provides an explanation of the presence of the ring of spacing 3.13 Å. in the transmission photograph of oxide withdrawn

* This has been confirmed by an X-ray examination which it is hoped will be published shortly.

TABLE III.

Electron Diffraction Photographs from Molten Lead.

X-ray (Levi).			(a).		(b).		(c).		(d).		(e).		(f).		(g).		(h).	
hkl.	I.	d.	d.	I.	d.	I.	d.	I.	d.	I.	d.	I.	d.	I.	d.	I.	d.	I.
101	vs	3.11	3.06	s	3.08	s	3.16	s	3.17	m	3.12	s	3.17	s	3.12	s	3.17	s
110	m	2.80	2.72	m	2.76	m	2.79	w	2.86	m	2.80	m	2.86	m	2.80	m	2.86	m
002	2.67	m	2.67	2.67	..
200	m	2.50	2.42	mw	2.50	m	2.43	m	2.50	..	2.43	m	2.50	..
112	w	1.98	2.00	w	1.98	w	1.90	w	1.98	m	1.98	m	1.98	..	1.98	..	1.98	..
112	s	1.86	1.81	w	1.85	w	1.85	w	1.85	..	1.88	..	1.85	..	1.88	..	1.85	..
211	s	1.67	1.63	?w	1.86	m	1.64	s	1.67	m	1.69	m	1.67	..	1.83	m	1.90	m
202	vs	1.55	1.53	?w	1.67	s	1.64	s	1.67	..	1.69	..	1.67	..	1.83	mw	1.64	m
103	1.50
220	w	1.40	1.52	m	1.52
301	..	1.28	1.27	w	1.41	m	1.41
310
004	w	1.25
222
213	s	1.22	1.19	?w	1.21	w	1.22	w	1.25	1.25	w
114	mw	1.14	1.13	w	1.13
312	mw	1.12	1.12	mw	1.10	w
321	w	1.07	1.07	mw
204	..	1.06
303	..	1.03
400	..	0.99	1.01	w	1.01
$a=3.97$ $ac=5.01$			$a=3.89 \pm 0.05$ $c=1.26$	3.89 ± 0.05 1.26	3.94 ± 0.01 1.26	3.94 ± 0.06 1.26	3.99 ± 0.04 1.26	3.98 ± 0.04 1.26	3.91 ± 0.03 1.26	3.99 ± 0.12 1.26								

from the metal on a loop to which could be assigned the indices (101) of the tetragonal structure. It has been mentioned above that in every case the lead showed rings immediately after fusion. These rings are almost certainly due to the oxide film which forms on the metal at room temperature, and the investigation shows that this film is of the tetragonal type. Before we can definitely assert that the first-formed film on the liquid metal has this structure it would be necessary to obtain a drop which was so clean that it showed no rings at all, and then study the pattern produced by oxidation. The orthorhombic structure found in the material withdrawn from lead melted in air and in the fused foil is formed under quite different conditions, both pressure of oxygen and temperature being higher than in the case of the drops in the electron diffraction apparatus. There is one observation which suggests rather strongly that the experiments carried out do show that the first-formed film at low temperatures and pressures is tetragonal. This is the fact that on fusion the drop is always very mobile and that the ring pattern obtained in this condition is identical with that obtained when the mobility is greatly reduced by oxidation. If the initial mobility of a drop which shows rings (and sometimes visible patches of oxide formed on the solid lump before fusion) is due to lack of continuity of the film, and if subsequent oxidation of the molten metal heals the gaps in the film and so gives the drop an apparent rigidity, then it would have been expected that in some photographs the structure of this new film would have produced detectable rings. Their absence suggests that it has the same structure as the existing discontinuous film, which, according to the evidence given above, is almost certainly the tetragonal type of oxide.

Acknowledgments.

We have great pleasure in acknowledging our debt to Dr. C. H. Desch, Superintendent of the Metallurgy and Chemistry Department, The National Physical Laboratory, for his interest in and encouragement of this work. Our thanks are due to Mr. J. Trotter for his assistance in the experimental work.

11th July, 1934.

XIII. *Toroidal Functions and the Complete Elliptic Integrals.* By J. R. AIREY, D.Sc., Sc.D.*

TOROIDAL functions, which satisfy Laplace's equation and are suitable for conditions over the surfaces of anchor-rings, were first investigated by C. Neumann, W. M. Hicks ⁽¹⁾, F. W. Dyson ⁽²⁾, and others. Papers have recently appeared by F. E. Relton ⁽³⁾ and V. Fock ⁽⁴⁾, in which the desirability of tabulating these Legendre functions of half odd integral order was emphasized. Fock suggests that the tabulation of the toroidal functions should be through the hypergeometric functions, in terms of which they can be expressed. A more convenient and accurate method, especially when the argument is large, is through the complete elliptic integrals of the first and second kind.

The tesseral toroidal functions, $y = P_{m,n}(u)$, n the order and m the rank, using the notation of W. M. Hicks, satisfy the differential equation

$$\frac{d^2y}{du^2} + \coth u \frac{dy}{du} - \left[(n^2 - \frac{1}{4}) + \frac{m}{\sinh^2 u} \right] y = 0.$$

These reduce to zonal functions when $m=0$, to sectorial functions when $n=0$.

The zonal toroidal functions of the two kinds are here denoted by

$$P_n(u) = \int_0^\pi \frac{d\theta}{(\cosh u - \sinh u \cos \theta)^{\frac{2n+1}{2}}}$$

and

$$Q_n(u) = \int_0^\infty \frac{d\theta}{(\cosh u + \sinh u \cosh \theta)^{\frac{2n+1}{2}}}.$$

In the particular cases, where $n=0$ and $n=1$, it has been shown ⁽¹⁾ that

$$P_0(u) = 2\sqrt{k'} \cdot K = 2e^{-\frac{u}{2}} \cdot K,$$

$$P_1(u) = \frac{2}{\sqrt{k'}} \cdot E = 2e^{\frac{u}{2}} \cdot E,$$

* Communicated by the Author.

$$\text{and} \quad Q_0(u) = 2\sqrt{k'} \cdot K' = 2e^{-\frac{u}{2}} \cdot K',$$

$$Q_1(u) = \frac{2}{\sqrt{k'}} \cdot (K' - E') = 2e^{\frac{u}{2}} (K' - E'),$$

where K and E are the complete elliptic integrals of the first and second kind, k^2 , the square of the modulus.

$$k^2 = \frac{2 \sinh u}{\cosh u + \sinh u} = 1 - e^{-2u},$$

$$k'^2 = \frac{1}{(\cosh u + \sinh u)^2} = e^{-2u}.$$

Here the argument u of the toroidal functions corresponds to the argument θ of the zonal spherical harmonics of integer order ⁽⁵⁾.

Extensive tables of the complete elliptic integrals have been constructed by Hayashi ⁽⁶⁾ and Milne-Thomson ⁽⁷⁾, argument k^2 . For values of k^2 less than 0.9, interpolated values, to nine or ten places, may be calculated without difficulty, *i. e.* for values of the argument u less than unity for the P-functions and greater than unity for the Q-functions. When k^2 lies between 0.9 and 1.0, the elliptic integrals are readily calculated from Tables I. and II.

The formulæ for K and E , due to Legendre ⁽⁸⁾, were used in computing these tables, the range of the argument k^2 for K , 0.830 to 1.000, and for E , 0.900 to 1.000: h is written for the square of the complementary modulus k'^2 .

$$K(k^2) = \log_e \frac{4}{\sqrt{h}} \cdot K_1 - K_2,$$

where

$$K_1 = \left\{ 1 + \frac{1^2}{2^2} \cdot h + \frac{1^2 \cdot 3^2}{2^2 \cdot 4^2} \cdot h^2 + \frac{1^2 \cdot 3^2 \cdot 5^2}{2^2 \cdot 4^2 \cdot 6^2} \cdot h^3 + \dots \right\}$$

and

$$K_2 = \left\{ \frac{1^2}{2^2} \left(\frac{2}{1} - \frac{2}{2} \right) \cdot h + \frac{1^2 \cdot 3^2}{2^2 \cdot 4^2} \left(\frac{2}{1} - \frac{2}{2} + \frac{2}{3} - \frac{2}{4} \right) \cdot h^2 + \dots \right\}.$$

$$E(k^2) = \log_e \frac{4}{\sqrt{h}} \cdot E_1 + E_2,$$

where

$$E_1 = \left\{ \frac{1}{2} \cdot h + \frac{1^2 \cdot 3}{2^2 \cdot 4} \cdot h^2 + \frac{1^2 \cdot 3^2 \cdot 5}{2^2 \cdot 4^2 \cdot 6} \cdot h^3 + \dots \right\}$$

and

$$E_2 = \left\{ 1 - \frac{1}{2} \left(\frac{1}{1} - \frac{1}{2} \right) \cdot h - \frac{1^2 \cdot 3}{2^2 \cdot 4} \cdot \left(\frac{2}{1} - \frac{2}{2} + \frac{1}{3} - \frac{1}{4} \right) \cdot h^2 - \dots \right\}.$$

Glaisher ⁽⁹⁾ appears to have been the first to suggest k^2 as the argument of the elliptic integrals and the Jacobian elliptic functions: "The quantities K , E , like the elliptic functions $\text{sn } u$, $\text{cn } u$ themselves, are rational functions of k^2 , and it is more proper to regard them as functions of k^2 than of k ."

The tables are given to ten or more decimal places with second differences*.

Starting with the values of $P_0(u)$, $P_1(u)$, $Q_0(u)$, $Q_1(u)$, functions of higher order and rank can be derived from the recurrence formulæ ⁽¹⁾, argument u understood:

$$(2n+1)P_{n+1} - 4nC \cdot P_n + (2n-1)P_{n-1} = 0,$$

$$P_{m \cdot n+1} - C \cdot P_{m \cdot n} - S \cdot P_{m+1 \cdot n} = 0,$$

$$(2m+1+2n)P_{m \cdot n+1} + (2m-1-2n)(C \cdot P_{m \cdot n} + S \cdot P_{m-1 \cdot n}) = 0,$$

$$(2m+1-2n)(P_{m \cdot n-1} - C \cdot P_{m \cdot n}) - (2m+1+2n)S \cdot P_{m+1 \cdot n} = 0,$$

$$(2m+1-2n)P_{m \cdot n-1} + (2m-1+2n)C \cdot P_{m \cdot n} + (2m-1-2n)S \cdot P_{m-1 \cdot n} = 0,$$

and two formulæ when m or n is constant:

$$(2m+1+2n)P_{m \cdot n+1} - 4nC P_{m \cdot n} + (2n-1-2m)P_{m \cdot n-1} = 0,$$

$$(2m+1+2n)S \cdot P_{n \cdot m+1} + 4mC P_{n \cdot m} + (2m-1-2n)S \cdot P_{n \cdot m-1} = 0.$$

In these formulæ C stands for $\cosh u$, S for $\sinh u$.

G. Witt's formulæ and tables ⁽¹⁰⁾ provide for the calculation of K and E to seven or eight significant figures. Over the range $60^\circ < \theta < 89^\circ 45'$, *i. e.* $0.75 < k^2 < 0.9948$,

$$k = \sin \theta \text{ and } \sin \theta_1 = \tan^2 \frac{\theta}{2},$$

$$K = \sec^2 \frac{\theta}{2} \cdot \sec \frac{\theta_1}{2} \cdot \sqrt{\sec \theta_1} \cdot C_1(\theta_1),$$

$$E = \cos^4 \frac{\theta}{2} [2L(\theta_1) - \cos^2 \theta_1] K,$$

and
$$L(\theta_1) = \cos^4 \frac{\theta_1}{2} \cdot C_2(\theta_1),$$

* The colon : represents approximately half a unit in the last decimal place, *e. g.* $K_2(0.010) = 0.00251 \ 65276(5)$

TABLE I.

Complete Elliptic Integral of the First Kind.

$$K = K_1 \log_e \frac{4}{\sqrt{h}} - K_2.$$

$h.$	$K_1.$	$\delta^2.$	$K_2.$	$\delta^2.$
0.00000	I.00000 00000 000	281	0.00000 00000 000	328
1	0 25000 141	281	0 25000 164	328
2	0 50000 563	281	0 50000 656	328
3	0 75001 266	281	0 75001 477	328
4	1 00002 250	281	1 00002 625	328
0.00005	I.00001 25003 516	281	0.00001 25004 102	328
6	1 50005 063	281	1 50005 907	328
7	1 75006 891	281	1 75008 039	328
8	2 00009 001	281	2 00010 501	328
9	2 25011 391	281	2 25013 290	328
0.00010	I.00002 50014 063	281	0.00002 50016 407	328
0.0000	I.00000 00000 00	2813	0.00000 00000 00	3281
1	02 50014 06	2813	02 50016 41	3282
2	05 00056 26	2814	05 00065 63	3283
3	07 50126 59	2814	07 50147 69	3283
4	10 00225 06	2815	10 00262 58	3284
0.0005	I.00012 50351 68	2815	0.00012 50410 31	3285
6	15 00506 46	2816	15 00590 89	3286
7	17 50689 40	2817	17 50804 32	3286
8	20 00900 50	2817	20 01050 62	3287
9	22 51139 78	2818	22 51329 78	3288
0.0010	I.00025 01407 23	2818	0.00025 01641 83	3288
0.000	I.00000 00000	2812	0.00000 00000	3282
01	025 01407 :	2818	025 01642	3289
02	050 05632 :	2824	050 06572	3296
03	075 12682 :	2830	075 14798	3303
04	100 22563	2836	100 26327 :	3311
0.005	I.00125 35279	2842	0.00125 41167	3318
06	150 50837	2848	150 59324	3325
07	175 69243	2854	175 80806	3333
08	200 90503	2860	201 05620 :	3340
09	226 14623	2866	226 33775	3347
0.010	I.00251 41609	2872	0.00251 65276 :	3355
11	276 71467	2878	277 00133	3362
12	302 04203	2884	302 38351	3370
13	327 39823	2891	327 79939	3377
14	352 78333 :	2897	352 24904	3385

TABLE I. (cont.).

h .	K_1 .	δ^2 .	K_2 .	δ^2 .
0.015	1.00378 19740 :	2903	0.00378 73254 :	3392
16	403 64049 :	2909	404 24996 :	3400
17	429 11267	2915	429 80139	3407
18	454 61400	2921	455 38688	3415
19	480 14453 :	2928	481 00653	3423
0.020	1.00505 70434	2934	0.00506 66040	3431
21	531 29348	2940	532 34858	3438
22	556 91202	2946	558 07113 :	3446
23	582 56001	2952	583 82816	3453
24	608 23753	2959	609 61971	3461
0.025	1.00633 94463	2965	0.00635 44588	3469
26	659 68138	2972	661 30674 :	3477
27	685 44784	2978	687 20238	3485
28	711 24408	2984	713 13286 :	3493
29	737 07015	2991	739 09828	3501
0.030	1.00762 92612 :	2997	0.00765 09870	3509
31	788 81206 :	3004	791 13421	3517
32	814 72804	3010	817 20488 :	3524
33	840 67411 :	3016	843 31080 :	3533
34	866 65035	3023	869 45205 :	3541
0.035	1.00892 65681	3029	0.00895 62871	3549
36	918 69356	3036	0921 84086	3557
37	944 76066 :	3042	0948 08857 :	3565
38	970 85819	3049	0974 37194	3573
39	996 98621	3055	1000 69104	3581
0.040	1.01023 14478	3062	0.01027 04595	3589
41	049 33397	3069	053 43675 :	3598
42	075 55385	3076	079 86354 :	3606
43	101 80448 :	3082	106 32639	3615
44	128 08594	3089	132 82538	3623
0.045	1.01154 39827 :	3096	0.01159 36060	3631
46	180 74157	3102	185 93212 :	3640
47	207 11589	3109	212 54005	3648
48	233 52130	3116	239 18445	3656
49	259 95787	3123	265 86541	3665
0.050	1.01286 42566	3130	0.01292 58302	3673
51	312 92475	3137	319 33735 :	3681
52	339 45520 :	3143	346 12850 :	3690
53	366 01709	3150	372 95656 :	3698
54	392 61047	3157	399 82161	3707
0.055	1.01419 23543	3164	0.01426 72372	3716
56	445 89203	3171	453 66300	3724
57	472 58034	3178	480 63952	3733
58	499 30043	3185	507 65337 :	3742
59	526 05237	3192	534 70465	3751

TABLE I. (*cont.*).

h .	K_1 .	δ^2 .	K_1 .	δ^2 .
0.060	1.01552 83623 :	3199	0.01561 79343	3760
61	579 65209	3207	588 91981	3768
62	606 50000 :	3214	616 08387	3777
63	633 38006	3221	643 28570	3786
64	660 29231	3228	670 52539	3795
0.065	1.01687 23685	3235	0.01697 80303 :	3804
66	714 21373	3242	725 11871	3813
67	741 22303	3249	752 47252	3822
68	768 26483 :	3256	779 86454	3831
69	795 33920	3264	807 29487 :	3840
0.070	1.01822 44620	3271	0.01834 76360	3849
71	849 58591 :	3278	862 27082	3858
72	876 75841	3286	889 81661	3867
73	903 96377	3293	917 40107	3876
74	931 20205 :	3301	945 02430	3885
0.075	1.01958 47335	3308	0.01972 68638	3894
76	1985 77773	3316	2000 38740 :	3904
77	2013 11526	3323	2028 12746 :	3914
78	2040 48602	3331	2055 90666	3923
79	2067 89009	3338	2083 72508	3932
0.080	1.02095 32753	3346	0.02111 58281 :	3941
81	122 79843	3353	139 47996	3951
82	150 30286	3361	167 41661 :	3960
83	177 84090	3369	195 39286 :	3970
84	205 41262	3377	223 40881	3979
0.085	1.02233 01811	3383	0.02251 46455	3989
86	260 65743	3392	279 56017	3998
87	288 33067	3398	307 69577 :	4008
88	316 03789	3408	335 87145 :	4018
89	343 77919	3414	364 08731	4027
0.090	1.02371 55463	3423	0.02392 34343 :	4037
91	399 36430	3431	420 63992 :	4047
92	427 20827	3438	448 97689	4056
93	455 08662	3446	477 35441	4066
94	482 99944	3454	505 77259	4076
0.095	1.02510 94679	3462	0.02534 23153 :	4086
96	538 92876	3470	562 73133 :	4096
97	566 94543 :	3478	591 27209	4106
98	594 99688 :	3486	619 85391	4116
99	623 08319	3494	648 47687 :	4126
0.100	1.02651 20444	3503	0.02677 14110	4136
01	679 36071	3510	705 84668	4146
02	707 55207 :	3518	734 59372	4156
03	735 77863	3526	763 38232	4166
04	764 04044	3534	792 21257	4176

TABLE I. (cont.).

h .	K_1 .	δ^2 .	K_2 .	δ^2 .
0.105	1.02792 33760	3543	0.02821 08459 :	4186
06	820 67019	3551	849 99848	4197
07	849 03829	3559	878 95433	4207
08	877 44198	3567	907 95225	4217
09	905 88134 :	3576	936 99234 :	4228
0.110	1.02934 35647	3584	0.02966 07472	4238
11	2962 86744	3593	2995 19947 :	4249
12	2991 41434	3601	3024 36671 :	4259
13	3019 99724 :	3610	3053 57654	4270
14	3048 61625	3618	3082 82907	4280
0.115	1.03077 27143	3627	0.03112 12439 :	4291
16	105 96288	3635	141 46263	4302
17	134 69068	3644	170 84388	4312
18	163 45492	3652	200 26825	4322
19	192 25567 :	3661	229 73584 :	4333
0.120	1.03221 09304	3670	0.03259 24677	4344
21	249 96710	3678	288 80115	4355
22	278 87794	3687	318 39907	4366
23	307 82565	3696	348 04066	4377
24	336 81031	3705	377 72601	4388
0.125	1.03365 83202	3714	0.03407 45524	4399
26	394 89086	3722	437 22846	4410
27	423 98692	3731	467 04578	4421
28	453 12029	3740	496 90730	4432
29	482 29105 :	3749	526 81315	4443
0.130	1.03511 49931	3758	0.03556 76342 :	4454
31	540 74514	3767	586 75824	4465
32	570 02863	3776	616 79771 :	4477
33	599 34989	3784	646 88195 :	4488
34	628 70898	3794	677 01107	4500
0.135	1.03658 10601 :	3803	0.03707 18518 :	4511
36	687 54108	3813	737 40440 :	4522
37	717 01427	3822	767 66884 :	4534
38	746 52566 :	3831	797 97862 :	4545
39	776 07536 :	3840	828 33385	4557
0.140	1.03805 66346 :	3849	0.03858 73465	4568
41	835 29005 :	3858	889 18113	4580
42	864 95522 :	3868	919 67341	4591
43	894 65907 :	3877	950 21160	4603
44	924 40169	3886	980 79582 :	4615
0.145	1.03954 18317	3896	0.04011 42620	4627
46	3984 00361	3905	042 10285	4639
47	4013 86310 :	3915	072 82589	4650
48	4043 76175	3924	103 59542 :	4662
49	4073 69963 :	3934	134 41159	4674

TABLE I. (*cont.*).

$h.$	$K_1.$	$\delta^2.$	$K_2.$	$\delta^2.$
0.150	1.04103 67686	3944	0.04165 27450	4687
51	133 69353	3953	196 18428	4699
52	163 74972	3963	227 14105	4711
53	193 84554	3973	258 14493	4723
54	223 98109	3983	289 19603	4735
0.155	1.04254 15646 :	3992	0.04320 29448 :	4747
56	284 37176	4002	351 44041	4759
57	314 62708	4012	382 63394	4771
58	344 92251	4022	413 87518	4784
59	375 25816	4031	445 16426	4797
0.160	1.04405 63413	4041	0.04476 50131 :	4809
61	436 05051	4052	507 88646	4821
62	466 50741	4062	539 31982	4834
63	497 00493 :	4072	570 80152	4847
64	527 54317	4082	602 33169	4860
0.165	1.04558 12222 :	4092	0.04633 91046	4873
66	588 74220	4102	665 53794 :	4886
67	619 40320	4112	697 21429	4898
68	650 10532	4123	728 93961	4911
69	680 84867 :	4133	760 71403 :	4924
0.170	1.04711 63336	4144	0.04792 53770	4937

TABLE II.

Complete Elliptic Integral of the Second Kind.

$$E = E_1 \log_e \frac{4}{\sqrt{h}} + E_2.$$

$h.$	$E_1.$	$\delta^2.$	$E_2.$	$-\delta^2.$
0.00000	0.00000 00000 00	38	1.00000 00000 00	41
1	0 50000 19	37	0.99999 74999 80	40
2	1 00000 75	38	9 49999 19	41
3	1 50001 69	37	9 24998 17	41
4	2 00003 00	38	8 99996 75	40
0.00005	0.00002 50004 69	37	0.99998 74994 92	41
6	3 00006 75	38	8 49992 69	40
7	3 50009 19	37	8 24990 05	41
8	4 00012 00	38	7 99987 00	41
9	4 50015 19	37	7 74983 55	40
0.00010	0.00005 00018 57	38	0.99997 49979 69	41

TABLE II. (cont.).

$h.$	$E_1.$	$\delta^2.$	$E_2.$	$-\delta^2.$
0.0000	0.00000 00000 0	375	1.00000 00000 0	406
1	05 00018 7 :	375	0.99997 49979 7	407
2	10 00075 0	375	94 99918 7 :	406
3	15 00168 8	375	92 49817 1 :	407
4	20 00300 1	375	89 99674 9	406
0.0005	0.00025 00468 9	375	0.99987 49492 0	407
6	30 00675 2 :	375	84 99268 4 :	407
7	35 00919 1 :	375	82 49004 2	406
8	40 01200 6	376	79 98699 3	407
9	45 01519 6	376	77 48353 6 :	407
0.0010	0.00050 01876 1 :	376	0.99974 97967 3 :	407
0.000	0.00000 00000	3752	1.00000 00000	4063
1	050 01875 :	3758	0.99974 97967 :	4072
2	100 07509	3764	949 91864	4080
3	150 16906 :	3771	924 81680 :	4088
4	200 30074 :	3779	899 67409 :	4097
0.005	0.00250 47021	3786	0.99874 49042	4105
6	300 67753 :	3793	849 26570	4114
7	350 92278	3800	823 99984	4122
8	401 20603	3807	798 69275 :	4131
9	451 52734	3814	773 34436 :	4140
0.010	0.00501 88680	3821	0.99747 95458	4148
1	552 28447	3828	722 52331 :	4157
2	602 72042	3836	697 05048	4165
3	653 19473 :	3843	671 53599	4174
4	703 70748	3851	645 97975	4183
0.015	0.00754 25873	3858	0.99620 38168	4192
6	804 84857	3865	594 74169	4201
7	855 47704 :	3873	569 05969	4210
8	906 14425	3880	543 33560	4219
9	956 85026	3887	517 56932	4228
0.020	0.01007 59514	3895	0.99491 76076	4236
1	058 37896 :	3902	465 90984	4245
2	109 20181 :	3910	440 01646	4254
3	160 06377	3917	414 08054	4263
4	210 96489	3925	388 10198	4272
0.025	0.01261 90526	3933	0.99362 08070	4282
6	312 88495	3940	336 01660	4291
7	363 90405	3947	309 90958 :	4300
8	414 96262	3955	283 75957 :	4309
9	466 06074	3963	257 56647	4318
0.030	0.01517 19849	3970	0.99231 33018 :	4328
1	568 37595	3978	205 05062	4337
2	619 59319	3985	178 72769	4346
3	670 85029	3993	152 36129 :	4355
4	722 14732 :	4001	125 95135	4365

TABLE II. (*cont.*).

h .	E_1 .	δ^2 .	E_2 .	$-\delta^2$.
0.035	0.01773 48437 :	4009	0.99099 49775	4375
6	824 86152	4017	9073 00040 :	4384
7	876 27883	4025	9046 45922	4393
8	927 73640	4033	9019 87411	4403
9	979 23429	4041	8993 24498	4413
0.040	0.02030 77259	4049	0.98966 57172	4422
1	082 35137	4057	939 85424	4431
2	133 97072	4065	913 09245 :	4441
3	185 63071	4073	886 28625 :	4450
4	237 33143	4080	859 43556	4460
0.045	0.02289 07295	4089	0.98832 54025 :	4470
6	340 85535 :	4097	805 60025	4480
7	392 67873	4105	778 61545	4489
8	444 54314 :	4113	751 58576	4499
9	496 44869	4121	724 51108	4509
0.050	0.02548 39544	4129	0.98697 39131	4519
1	600 38348	4137	670 22635 :	4529
2	652 41289 :	4146	643 01611	4539
3	704 48376 :	4154	615 76048	4549
4	756 59617	4162	588 45937	4559
0.055	0.02808 75019	4170	0.98561 11266 :	4569
6	2860 94592	4179	533 72028	4579
7	2913 18343	4187	506 28211	4589
8	2965 46280	4196	478 79806	4599
9	3017 78413	4203	451 26801 :	4608
0.060	0.03070 14750	4212	0.98423 69189	4618
1	122 55298	4220	396 06957	4629
2	175 00066 :	4229	368 40096	4639
3	227 49064	4238	340 68595 :	4650
4	280 02299	4246	312 92445 :	4660
0.065	0.03332 59780	4255	0.98285 11635 :	4670
6	385 21515	4263	257 26155 :	4681
7	437 87513	4271	229 35994 :	4691
8	490 57782	4280	201 41142	4701
9	543 32331 :	4288	173 41589	4712
0.070	0.03596 11170	4297	0.98145 37323 :	4723
1	648 94305 :	4306	117 28335	4733
2	701 81748	4315	089 14614 :	4744
3	754 73505	4324	060 96150	4754
4	807 69586	4333	032 72931 :	4765
0.075	0.03860 69999	4341	0.98004 44948	4775
6	3913 74753 :	4350	7976 12189	4786
7	3966 83858	4359	7947 74643 :	4797
8	4019 97321 :	4368	7919 32301	4808
9	4073 15153	4377	7890 85151	4819

TABLE II. (cont.).

h .	E_1 .	δ^2 .	E_2 .	$-\delta^2$.
0.080	0.04126 37361	4386	0.97862 33183	4829
1	179 63955	4395	833 76385	4840
2	232 94944	4404	805 14747	4851
3	286 30336 :	4413	776 48257	4862
4	339 70142	4422	747 76906	4873
0.085	0.04393 14369	4431	0.97719 00681	4884
6	446 63027	4440	690 19572	4895
7	500 16125 :	4450	661 33567 :	4906
8	553 73673	4459	632 42657	4917
9	607 35679 :	4468	603 46828	4928
0.090	0.04661 02153	4477	0.97574 46071 :	4940
1	714 73103	4486	545 40374 :	4951
2	768 48540	4495	516 29726	4962
3	822 28472	4505	487 14115 :	4974
4	876 12909	4514	457 93531	4985
0.095	0.04930 01860 :	4523	0.97428 67961	4996
6	4983 95336	4533	399 37395	5008
7	5037 93343	4543	370 01821	5020
8	5091 95893 :	4552	340 61227	5031
9	5146 02996	4561	311 15602	5042
0.100	0.05200 14660	4570	0.97281 64934	5053

with similar expressions for the range $89^\circ 45' < \theta < 90^\circ$. The factors $C_1(\theta_1)$ and $C_2(\theta_1)$ are given to eight decimals in the tables.

H. V. Lowry ⁽¹¹⁾ has found an expression suitable for calculating the elliptic integral K when the modulus k is nearly unity :

$$K = \frac{1}{1-k} \left[\left\{ 2 \log 2 - \log \left(\frac{1-k}{1+k} \right) \right\} \cdot F \left\{ \frac{1}{2} \cdot \frac{1}{2} \cdot 1 \cdot \left(\frac{1-k^2}{1+k^2} \right) \right\} - \left\{ \left(\frac{1}{2} \right)^2 \left(\frac{1-k}{1+k} \right)^2 + \left(\frac{1.3}{2.4} \right)^2 \left(1 + \frac{2}{3.4} \right) \left(\frac{1-k}{1+k} \right)^4 + \dots \right\} \right].$$

In terms of the θ elliptic functions,

$$K = \pi \theta_3^2(0)$$

and

$$E = K - \frac{1}{4K} \cdot \frac{\theta_0''(0)}{\theta_0'(0)}.$$

When k^2 is nearly unity,

$$\theta_3^2(0), \theta_0''(0)/\theta_0(0)$$

may be evaluated from the formulæ

$$\theta_3^2(0) = (1 + 4q_1 + 4q_1^2 + 4q_1^4 + 8q_1^5 + 4q_1^8 + 4q_1^9 + \dots)$$

and

$$\frac{\theta_0''(0)}{\theta_0(0)} = \frac{1}{\pi^2} \cdot \log_e q_1 \{ (1 + 8q_1^2 + 32q_1^4 - 40q_1^6 + 48q_1^8 - 32q_1^{10} \dots) + 2 \},$$

q_1 the nome corresponding to k'^2 , the square of the complementary modulus. This method, however, compares unfavourably with the one based on Legendre's series, especially in the case of the elliptic integrals of the second kind.

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XIV. *Notices respecting New Books.*

Isaac Newton : A Biography. By LOUIS TRENCHARD MORE.
[Pp. xii+675.] (New York and London : Charles Scribner's
Sons. Price 18s. net.)

THE bicentenary, on 20th March, 1927, of Sir Isaac Newton's death called attention to the fact that we have no satisfactory critical biography of the man who is still regarded as one of the greatest of scientific geniuses. The volume before us is an attempt to fill the gap.

As a start, Professor More (with the aid of Messrs. Sotheman & Co.) formed an almost complete collection of published works relative to his subject (in each edition when possible), and also a number of rare pamphlets and private notes of Newtonian scholars. Great help was afforded by the British Museum, the library of Congress, and also by the Directors of the Pierpont Morgan Library (for a copy of Newton's Memorandum Book which is one of the treasures of that collection). He was permitted to inspect and use all the Newton manuscripts in the University of Cambridge. Blanche, Lady Portsmouth and her nephew Viscount Lymington sent their priceless collection in Hurstbourne Park to the British Museum in order that he might examine and use it at his leisure. Also the custodian of the manuscripts in the Library in the Museum gave him every convenience and help during his weeks of work in copying the manuscript written in Newton's own clear handwriting. It should be mentioned that all Newton's papers were inherited by his niece, Catherine Conduit, whose daughter was the mother of the 2nd Earl of Portsmouth. These papers have remained in the family ever since, and are known as the Portsmouth Collection.

With the aid of these documents, together with Priestley's *Memoirs* (1855) and the bicentenary volume (Greenstreet, 1927), this biography has been written. In the small space at our disposal we propose to point out a few of its leading characteristics.

In the first place, the book is not written for physical experts and, consequently, any discussion of recondite matter is restricted. This will be regretted by many who, however, would be in the minority. It is a pity that some space was not allotted for this purpose (for example, a special appendix might have been provided), but probably the author concluded that that did not lie within his special province.

Professor More is to be congratulated on the very thorough investigations which he himself has made into some of the

more intricate biographic problems which arise. For example, Newton's first calculations of the attraction of the earth on the moon were laid aside and the subject incubated in his mind for twenty years before publication. He was by no means idle in the interim. In mathematics he had made important discoveries in the solution of problems by the new method of infinite series; he had edited Kinkhuysen's Algebra, discovered the binomial theorem, and invented fluxional calculus. He had accomplished an astounding amount of work on the subject of light, had prepared his Lucasian lectures, and had edited Varenius's Geography. The cause of the delay is very fully discussed. Probably the main reason was Newton's unwillingness to advance until he had extended the law of gravitation to apply to finite spheres as well as massive points. When once he had achieved this extension he became profoundly absorbed in his work, was scarcely conscious that he had eaten his meals, and took insufficient sleep until his work was completed.

Much of the detail has been given elsewhere in various places; but Professor More spares no pains in examining the available literature with the object of finding fresh evidence. "When he finally published his '*Principia*,' the world was amazed with the realisation that the new science, begun by Copernicus, had been brought to fruition, and that a new philosophy of life had been born."

The author has attempted to make the story more realistic by describing not only Newton, but also the personalities with whom he had to deal. This course is apt to become somewhat discursive and to produce a broken and confused narrative, but it undoubtedly assists in elucidating, for those who are not familiar with the personalities of the period, the interplay of Newton and his friends. Amongst these friends are the impetuous Hooke, the sagacious Halley, the astronomer Flamsteed, the philosopher John Locke, and the architect Christopher Wren. The quoted correspondence shows that things did not always go smoothly between them. However, perhaps too much importance is given by the biographer to the differences that arose. We may consider one case in particular. In a letter dated Nov. 24, 1679, Hooke tried to get into friendly correspondence with Newton, in which they might exchange and discuss philosophical questions. Newton (Nov. 28th) is not enthusiastic and professes that he had for some years been endeavouring to bend himself from philosophy to other studies. All the same he suggests an experiment for detecting the rotation of the earth. Hooke promptly reads the communication to the Royal Society on Dec. 4th, along with a criticism of his own, and communicates with Newton, who replies on the

13th Dec., admits the criticism and discusses the path of the falling body, but treats it as being of no moment. Hooke reads the letter to the Royal Society on Dec. 18th, together with a statement of a trial of the experiment, and writes again on Jan. 6, 1680. To this letter Newton does not give an answer, and Professor More infers that he was "thoroughly angry." We see no sure signs of such anger. It is safer to say that Newton wisely decided that the only way of dealing with the irrepressible Hooke was to keep silence. Eleven days later, Hooke, possibly suspecting that he has been too insistent, writes a very friendly letter asking for a continuance of their mutual discussions, but Newton still does not at once reply. It is not until the end of the year that he wrote to Hooke, "For the trials you made of an experiment suggested by me about falling bodies I am indebted to you, thanks for which I thought to have returned by word of mouth, but not having yet the opportunity must be content to do it by letter."

It is not till the 'Principia' is presented to the Royal Society *five or six years later*, and Halley reports to Newton (who was not present) that Hooke had made a scene in the Society (by claiming the discovery of the law of gravitation as his own and that credit was due to him), that Newton at last (June 1686) unbosoms himself to Halley in a letter which at least shows just indignation at Hooke's unjustifiable demands.

The mention of the last of the letters to Hooke and of this letter to Halley (which is given *undated*) are made in a different order by Professor More, and it is only with difficulty that the correct order (as above) can be appreciated. The change of order makes a great difference in the interpretation of the events. Instead of viewing Newton in a state of thorough anger for many years we find him writing a courteous letter to Hooke in less than twelve months.

When the outbreak occurred the wise Halley was able to smooth things over (at any rate for a time). He knew quite well that the London group had discussed the inverse-square law; he knew equally well that they had achieved nothing with it. Newton meanwhile had developed a new science.

The controversy with Leibniz on the invention of the Calculus has a chapter to itself. It is too technical a subject to be treated satisfactorily in a general biography, but Professor More succeeds in giving a general account of the controversy which will be found to be of great interest.

Newton was not to remain a Cambridge professor all his life. In 1695 it was decided that the coinage of the country should be completely reformed. A bill was drawn up by Montague, with the aid of Locke and Somers, providing for the change which began in the February of 1695/96. Montague obtained

for Newton the post of Warden of the Mint, and consequently Newton resigned his professorship and became a public servant in the following month. We are not told much about his duties. At ordinary times the post was possibly a sinecure, but abnormal work would arise in connexion with the coinage, which rose from 15 thousand to 120 thousand pounds-weight of silver per week. The politicals used the crisis to discredit the government, and serious disturbances broke out at Chester and elsewhere, where local branches of the Mint had been restarted. [Many branches had existed in olden times, but they had gradually been closed until in Mary's reign no branch existed. But some had been restarted to meet the new demands.] Whatever his duties were he apparently carried them out successfully, for at the end of the new coinage he was appointed as Master of the Mint, which was probably a more authoritative position. He kept this post till his death; thus he was at the Mint for more than thirty years.

His removal to London brought him into closer contact with the Royal Society. The publication of the '*Principia*' had placed him in a pre-eminent position in Science, and he was elected President of the Society on Nov. 30th, 1703. He remained President until his death 25 years later—a period of presidency which has only once been exceeded.

In closing this short notice we must express regret at the lack of sympathy which Professor More evinces for modern theory. He surely does not realize the vast amount of experimental work, all over the world, on which modern theories of "electron structures" are based.

Newton himself spent much time on the transmutation of metals. He would have been one of the first to enquire into the recent undoubted experimental successes in transmutation and, after having satisfied himself, to rejoice in the results.

Sir Isaac Newton's Mathematical Principles of Natural Philosophy and his System of the World. By FLORIAN CAJORI (late Professor of the History of Mathematics in the University of California.) [Pp. xxxv+680.] (Cambridge, at the University Press, 1934. Price 35s. net.)

PROFESSOR FLORIAN CAJORI, who was responsible for the conception of this volume, died (in 1930) before its completion. The final preparation for the press was undertaken by Mr. R. T. Crawford at the request of the University of California Press.

The book is essentially Andrew Motte's translation of Newton's '*Principia*' into English (made in 1729), together with '*Newton's System of the World*.' It appears that Cajori had long had the idea of revising Motte's work by

rendering certain technical phrases in a more modern form: for example, by changing "reciprocally in the subduplicate ratio of" into "inversely as the square root of"; changing "subsesquiplicate ratio" into " $2/3$ th [sic] power of the ratio" etc. In revising Motte's translation of Cote's Preface and of the 'Principia,' use has been made of R. Thorp's translation (Bk. I. 2nd edit., 1802). The geometric figures of the 'Principia' are taken from the 3rd edition (1726).

It is probable that Cajori had intended to write a preface, but none exists. An historical and explanatory appendix by him is included. This is quite good reading though rather restricted.

The portrait of Newton which forms the frontispiece is a photogravure made from a portrait gummed in vol. ii. of a large work entitled 'Heads in Taille Douce' (p. 128) which is in the Pepys Library at Cambridge. The portrait in 'Edleston' is an engraving from the same original. A facsimile of the title-page of the first edition of the 'Principia' is added.

Loud Speakers. Theory, Performance, Testing, and Design.

By N. W. McLACHLAN, D.Sc., A.M.I.E.E. [Pp. 399+xii.]
(Oxford Engineering Science Series, Clarendon Press.
Price 40s. net.)

THE literature of loud speakers has become very extensive, and its readers will know that the contributions of Dr. McLachlan form no small part of it. The present volume is to be welcomed as presenting the known facts about loud speakers in a very complete form, and comes opportunely at a time when strenuous efforts are being made by manufacturers to improve a component which is very often the least satisfactory one in a sound-reproducing equipment.

The first part of the book deals with the theory of sound propagation from vibrating surfaces. Bessel functions express the facts in problems of this kind, and we note in the preface that the author has written a book on this branch of mathematics for the benefit of those engineers who may wish to go fully into the theory given in the present work. The effect of baffles is examined very completely, and the section includes a concise account of the theory of horns.

Thereafter follow sections dealing with the driving mechanisms, and it is good to see a whole chapter on magnets.

The latter half of the book deals mainly with experimental work on which, at the present time, the principles of design largely rest. Included here we find methods of testing efficiency and electrical impedance, while an important chapter on the vibrational modes of conical shells gives the results of extensive

researches into the behaviour of conical diaphragms with various impressed frequencies and under impulse conditions.

In the concluding chapter on horn type speakers the author has some interesting things to say about the reproduction of higher frequencies. We find, for instance, that the fundamental vibrational mode of a halfpenny occurs at 12,000 cycles, and therefore the jingling of these coins provides a severe test of the reproducing qualities of a speaker. The author rightly points out that improvements in high-note reproduction reveal imperfections in the transmission system, but it is to be hoped that designers will not, on this account, remain content to confine the audible output to the lower and middle frequencies.

The book is to be warmly recommended to designers of apparatus for either domestic or public address and picture-theatre use.

The Diffraction of X-Rays and Electrons by Amorphous Solids, Liquids, and Gases. By J. T. RANDALL. [Pp. 290+xii.] (Chapman and Hall. Price 21s.)

IN so far as the diffraction of X-rays by amorphous matter is concerned, this book certainly satisfies a long-felt need. The subject is one which lies very near the border-line of what can be included in books dealing more generally with X-ray diffraction, and in consequence has usually been treated very briefly or not at all. The subject is also one which is specially difficult to study from the original papers, for these are very widely scattered; one has not only to search through journals of physics, chemistry, and crystallography, but also through journals of a more technical character, such as the 'Journal of the Textile Institute' and the 'Journal of the Society of Glass Technology.' This, of course, indicates the wide application, both scientific and technological, of X-ray and electron methods of investigating amorphous matter. The application of electron diffraction is more recent, but many results have already been obtained, and it is useful to have them linked up with results obtained in other ways.

The scope of the book is, briefly, as follows:—A preliminary chapter gives a highly condensed summary of X-ray method of crystal analysis. The diffraction of X-rays by exceedingly small crystals, such as colloidal particles, is then considered, and the difficulties of determining the sizes of such particles from the breadth of spectral lines is discussed; this is, perhaps, one of the most useful sections of the book, for much of the theoretical work on this subject is not easily accessible. From this we pass on to X-ray and electron diffraction by gases

and vapours and to a discussion of the information which has been obtained concerning molecular structure. The diffraction effects due to *elastic* scattering of electrons only are considered; a brief reference to the fact that diffraction effects can also be obtained with *inelastically* scattered electrons might also have been included, and a short explanation given of why this is possible when, in the case of crystals, X-rays scattered incoherently do not give diffraction effects. The next section of the book deals with X-ray diffraction by liquids; a very full survey is given of experimental and theoretical work in this field. Then follow two very interesting chapters; one gives an account of investigations of glasses (a subject to which Mr. Randall has himself contributed) and of various forms of carbon, while the other describes investigations of the structures of organic fibres such as hair, cotton, wool, and silk. The study of surface conditions, particularly by electron methods, is next considered, and finally a short account is given of the transition from the solid to the liquid state, and of the nature of liquid crystals.

This necessarily brief summary is sufficient to show that the book deals with every aspect of the subject indicated by the title. Lists of references to original papers are given at the ends of chapters, and should prove useful to readers wishing to study particular aspects of the subject in more detail. The book has been very nicely produced and is adorned by many admirable photographs; it is a comprehensive and yet very readable work, and can be recommended whole-heartedly to students and others interested in the subject.

Wave Mechanics: Advanced General Theory. By J. FRENKEL.
[Pp. viii+525.] (Oxford: Clarendon Press, 1934. Price 35s.)

THIS is the second part of Frenkel's 'Wave Mechanics,' of which the first, 'Elementary Theory,' was published in 1932. The work is carried out on generous lines. It is extremely comprehensive in respect of the number of general questions with which it deals and in the fullness of the exposition. The scheme adopted makes lengthiness inevitable, and though length is a very real drawback for many possible readers, the length has had the advantage of making the book unusually clear and comprehensible. The reader is not continually held up by missing steps in the arguments, and by going through this book he may gain a full and satisfying grasp of the subject. The book incorporates practically all the more important theoretical work, but

Frenkel has a complete mastery of his subject-matter and develops his theme in a manner which is individual in the best sense. As a piece of continuous detailed exposition the book is a remarkable achievement.

The title 'Wave Mechanics' is, in a sense, an understatement. Rather the book is a treatise on quantum mechanics generally approached from the wave mechanical side. After the connecting-links between wave and classical mechanics have been considered operator and matrix methods and general transformation theory are successively treated, there being an excellent section on geometrical representation. Perturbation theory is developed as a special case of transformation theory. These chapters are concerned with non-relativistic formulations of the theory. The relativistic remodelling and the magnetic generalization of wave mechanics are then taken up, and a detailed account is given of the Dirac theory of the electron. Problems of many particles are discussed, and finally an account is given of the attempts made to develop a quantum electrodynamics.

It is characteristic of the treatment that Frenkel takes the various more particularized theoretical topics as it were in his stride, incorporating them smoothly in his general scheme. The book is written in a pleasant flowing style, the most recondite theoretical questions being discussed in an engagingly calm and straightforward way. As to the manner in which Frenkel has carried out his design there can be nothing but admiration. The design, however, is such that little help is given to the reader who may wish to refer to the book for particular points. In keeping with this the index "does not make any claim at completeness." Consisting of one page for a book of over five hundred pages it could not well do so. It is to be hoped that the third volume of the trilogy will be furnished with an index of the whole which is less ludicrously inadequate. The reader who wishes to gain a full and detailed grasp of quantum mechanical theory could, however, have no better guide than is provided by this book.

The volume, in common with some others in the same series, seems unnecessarily heavy; apart from this, it is admirably produced, and the printing is beyond praise.

[The Editors do not hold themselves responsible for the views expressed by their correspondents.]

FIG. 1.

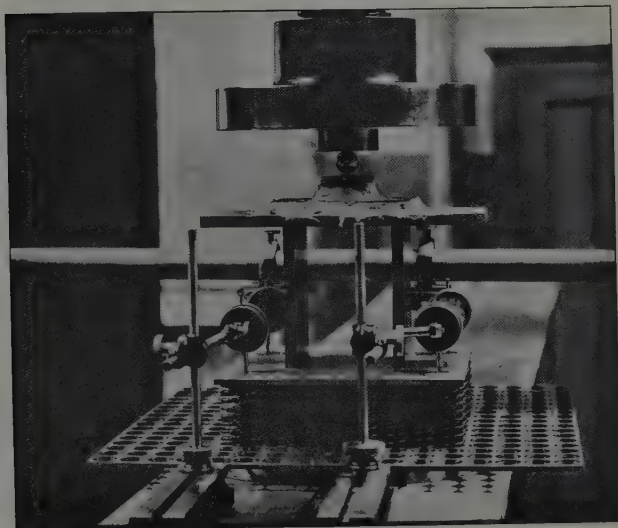


FIG. 2.

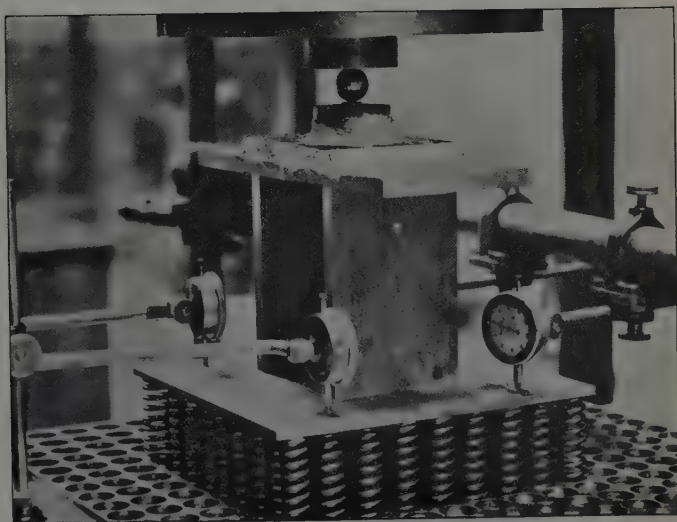
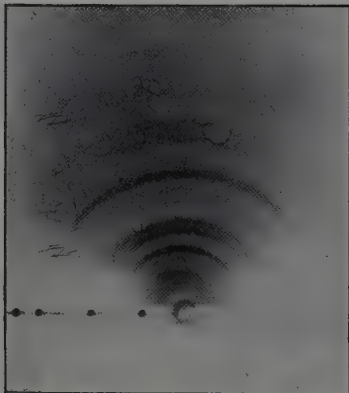
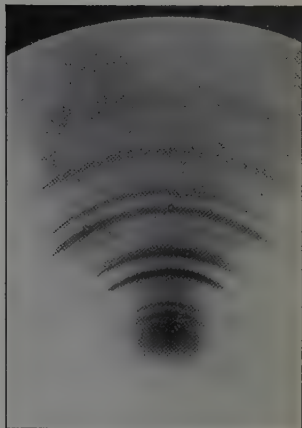


FIG. 1.



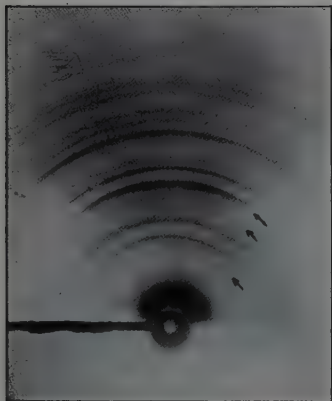
The fresh layer.

FIG. 2.



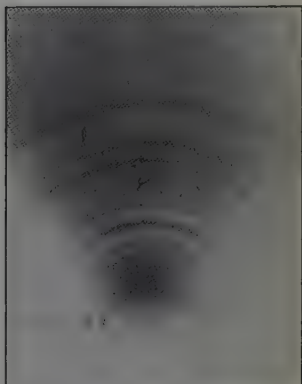
The activated layer.

FIG. 3.



Layer with superfluous rings.

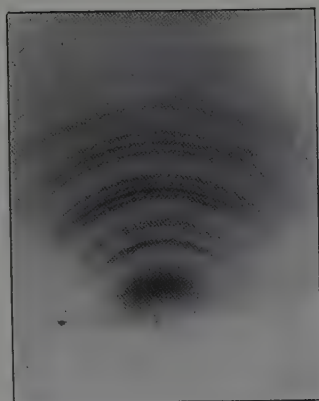
FIG. 4.



The hexagonal structure.

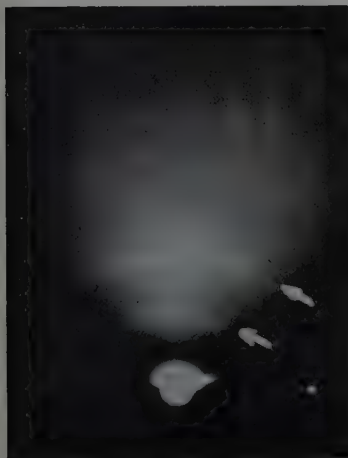
Electron diffraction patterns taken from oxide-coated filaments (see fig. 5 as well).

FIG. 5.



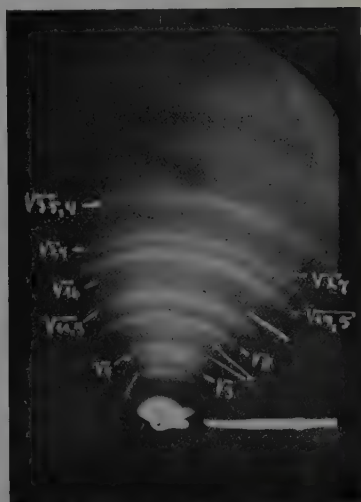
Tetragonal structure.

FIG. 6.



Beilby layer.

FIG. 7.



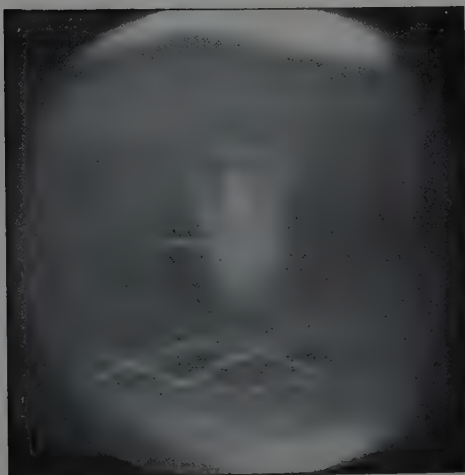
NiO pattern with forbidden rings.

Electron diffraction patterns taken from the surface of a nickel block,

FIG. 2.

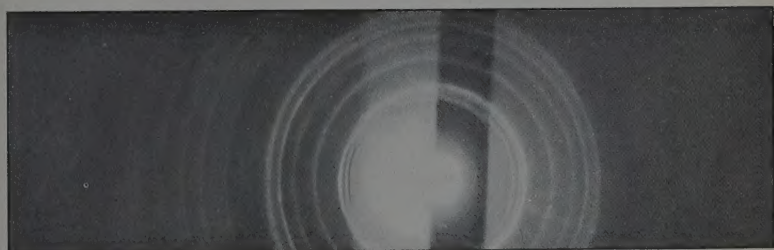


(a) No electric field. $\times 13.4$.



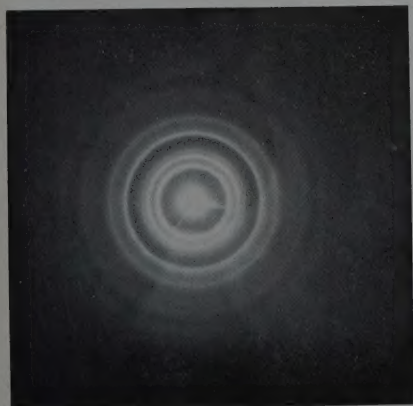
(b) Alternating field; $60\sim, 3000\text{ V/cm}$. $\times 13.4$.

FIG. 2.



Zinc oxide "smoke" condensed on copper wire.

FIG. 3.



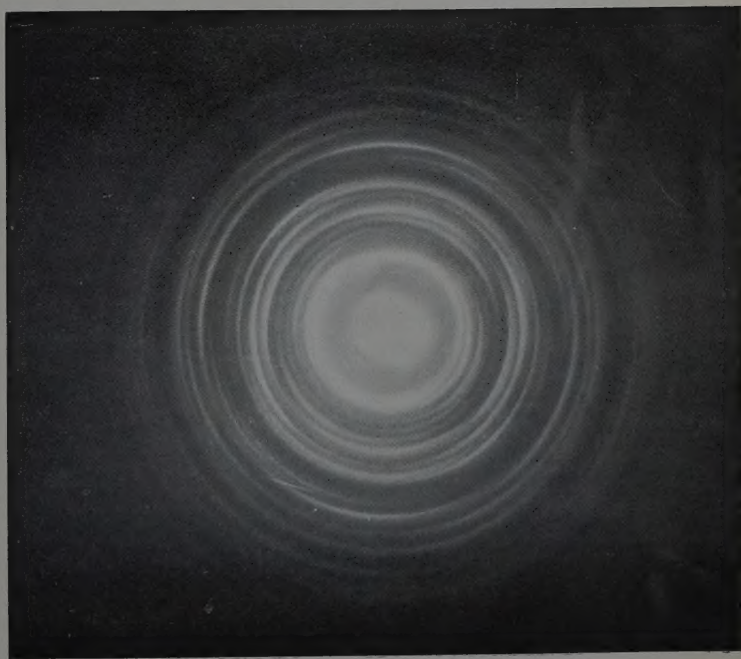
SnO_2 "transmission" method.

FIG. 4.



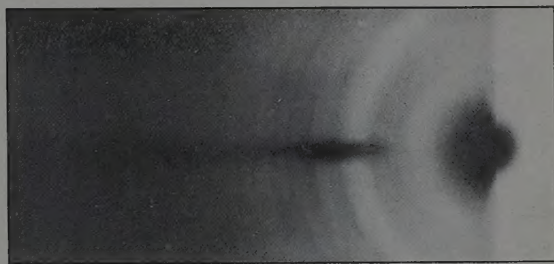
SnO_2 on surface of molten tin drop.

Fig. 5.



Orthorhombic (yellow) PbO "transmission" method.

Fig. 6.



Tetragonal (red) PbO on surface
of molten lead.

